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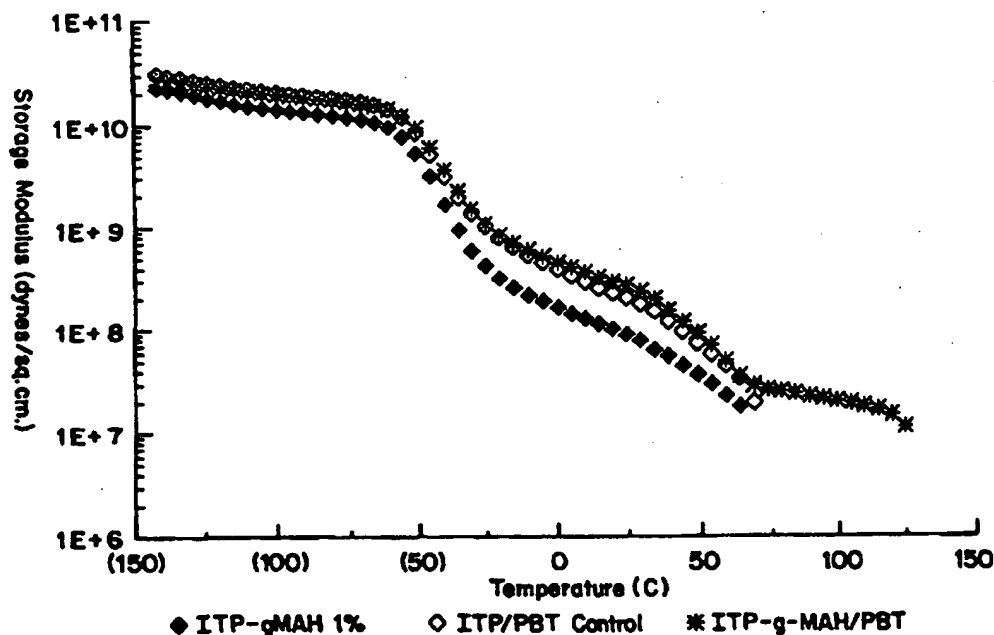
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(71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).			
(72) Inventors; and (75) Inventors/Applicants (for US only): FARAH, Hani [US/US]; 2702 Field Line Drive, Sugarland, TX 77479-1417 (US). LAUGHNER, Michael [US/US]; 1403 North Road, Lake Jackson, TX 77566-3616 (US). HOFMEISTER, Frank [US/US]; 405 Griffin Road, Greenville, SC 29607 (US). HO, Thoi, H. [US/US]; 54 Orchid Court, Lake Jackson, TX 77566 (US). HUGHES, Morgan [US/US]; 708 Milton Street, Angleton, TX 77515-3449 (US). PHAM, Hoang, T. [US/US]; 707 Walnut Street, Lake Jackson, TX 77566-3616 (US). NAMHATA, Sarada, P. [IN/NL]; Klaprooslaan 70, NL-Terneuzen (NL). BOSNYAK, Clive, P. [US/US]; 4171 Springhill Road, Midland, MI 48642 (US). JOHNSTON, Robert, T. [US/US]; 117 Fawn Trail, Lake Jackson, TX			

(54) Title: BRANCHED BLOCK ETHYLENE POLYMERS, THEIR PREPARATION AND COMPOSITIONS COMPRISING THE SAME



(57) Abstract

Branched block ethylene polymers prepared from a narrow ethylene polymer, an ethylenically unsaturated functionalized organic compound, and reactive thermoplastic polymer, and methods of preparing such branched block ethylene polymers, are useful to prepare an impact modified ethylene polymer.

rubbers such as ethylene/propylene copolymer. These added substances are capable of improving the resistance of polycarbonate to solvents, but they tend to delaminate and cause an offsetting reduction in the toughness, impact resistance and weldline strength of the blended polycarbonate composition. Such delamination, and the resulting loss of utility, is reported, for example, in US-A-4,496,693.

Impact resistance in polycarbonate can be improved by the incorporation of emulsion or core-shell elastomers such as methacrylate/butadiene/styrene copolymer or a butyl acrylate rubber. However, these core-shell rubbers hinder processability of the blend by increasing viscosity, and impart no improvement to the solvent resistance of polycarbonate. It would accordingly be desirable if modifiers, particularly olefin-based modifiers, blended with thermoplastics such as polycarbonate for the purpose of improving solvent resistance did not also deleteriously affect toughness and impact and weldline strength, and cause delamination as evidenced by peeling or splintering in a molded article.

US-A-5,346,963 discloses ethylene polymers which are grafted with an ethylenically unsaturated compound, and discloses blends of such grafted ethylene polymers with compatible thermoplastics. The description of the graft-modified ethylene polymers in this reference does not, however, mention a branched block ethylene polymer as defined herein.

US-A-5,300,574 discloses that crosslinking is reduced when maleic anhydride is grafted onto a saturated ethylene polymer if the grafting reaction is conducted in the presence of a polyamide. However, this reference does not mention a branched block ethylene polymer.

Hughes, et al. in U.S. Patent 5,346,963 disclose substantially linear polyethylenes grafted with one or more unsaturated organic compounds containing both ethyleneic unsaturation and a carbonyl group in thermoplastic blends as compatibilizers for filled polymers, and as impact modifiers for other polyolefins and a polyamide.

BRANCHED BLOCK ETHYLENE POLYMERS, THEIR PREPARATION AND COMPOSITIONS  
COMPRISING THE SAME

Field of the Invention

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This invention relates to ethylene polymers, more specifically block polymers of ethylene polymers, compositions containing block ethylene polymers, methods for the preparation of such block ethylene polymers and for compositions containing such block ethylene polymers.

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Background of the Invention

The graft-modification of an ethylene polymer with various olefinically unsaturated monomers is well known in the art. Such modification renders an essentially nonpolar polymer material

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compatible, at least to some limited extent, with a polar material.

However, graft-modification can have a detrimental impact on one or more other properties of an ethylene polymer. For example, USP

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4,134,927, 3,884,882 and 5,140,074 all report undesirable changes in rheological properties due to cross-linking of a graft-modified material. These changes ultimately impact the processibility of the material and, thus, its utility in commercial applications.

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In addition, when it is desired to blend an ethylene polymer with another molding polymer, graft-modification of the ethylene polymer, which may be beneficial in the context of adhesiveness, may adversely affect the compatibility of the ethylene polymer with the blending or molding polymer. It would accordingly be desirable if an ethylene polymer could be modified in such manner that its

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compatibility with other polymers in a blend is not adversely affected while other properties of the ethylene polymer (and preferably the resulting blend), such as its rheology, are improved.

An additional and particular challenge which has confronted industry is the improvement of the properties of polycarbonate. This disadvantage has been somewhat relieved by the practice of blending polycarbonate with various olefin polymers such as low density polyethylene or linear low density polyethylene, or thermoplastic

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a reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated organic compound, said method comprising

- 5 (1) forming the ethylenically unsaturated functionalized organic compound into a branch off of the ethylene polymer to form a branched ethylene polymer, and thereafter
- (2) reacting the reactive thermoplastic polymer with the branched ethylene polymer to form the branched block ethylene polymer.

10 In a preferred aspect, this invention involves a method of preparing a branched block ethylene polymer which comprises

- (a) a homogeneous ethylene polymer which preferably has:
  - 15 (i) a  $M_w/M_n$  ratio, as determined by gel permeation chromatography, of less than about 3.0;
  - (ii) a density of about  $0.93 \text{ g/cm}^3$  or less; and
  - 20 (iii) a Short Chain Branching Distribution Index of greater than about thirty percent;
- (b) an ethylenically unsaturated functionalized organic compound; and
- (c) a reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated functionalized organic compound;

25 said method comprising (1) forming the ethylenically unsaturated functionalized organic compound into a branch off of the homogeneous ethylene polymer to form a branched homogeneous ethylene polymer, and thereafter (2) reacting the reactive thermoplastic polymer with the branched homogeneous ethylene polymer to form the branched block ethylene polymer.

30 In yet another aspect, this invention involves a composition comprising a blend of a thermoplastic blending or molding polymer with a branched block ethylene polymer, wherein the branched block ethylene polymer comprises

- (a) an ethylene polymer;
- 35 (b) an ethylenically unsaturated organic compound; and

One of the objects of this invention is to prepare an ethylene-based polymer which has improved viscoelastic behavior, and which, when used as a modifier in a blend with a thermoplastic molding polymer, imparts to such blend a desirable balance of improved rheological behavior, good impact resistance, transparency in thin sections and films, surface hardness, and reduced notch sensitivity. This object, and others disclosed below, is attained by the preparation of a branched block ethylene polymer and the use of such branched block ethylene polymer in the compositions of this invention.

10 Summary of the Invention

In one aspect, this invention involves a branched block ethylene polymer comprising

- (a) an ethylene polymer;
- (b) an ethylenically unsaturated functionalized organic compound;
- 15 and
- (c) a reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated functionalized organic compound to form the branched block ethylene polymer.

20 In a preferred aspect, this invention involves a branched block ethylene polymer comprising

- (a) a homogeneous ethylene polymer having:
  - (i) a  $M_w/M_n$  ratio, as determined by gel permeation chromatography, of less than about 3.0;
  - 25 (ii) a density of about 0.93 g/cm<sup>3</sup> or less; and
  - (iii) a Short Chain Branching Distribution Index of greater than about thirty percent;
- (b) an ethylenically unsaturated functionalized organic compound; and
- 30 (c) a reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated functionalized organic compound to form the branched block ethylene polymer.

In another aspect, this invention involves a method of preparing  
35 a branched block ethylene polymer which comprises an ethylene polymer, an ethylenically unsaturated functionalized organic compound and

determined by gel permeation chromatography, of less than about 3.0, a density of about 0.93 g/cm<sup>3</sup> or less; and a Short Chain Branching Distribution Index of greater than about thirty percent; an ethylenically unsaturated functionalized organic compound; and a  
5 reactive thermoplastic polymer, said method comprising:

- (1) forming a branched block ethylene polymer by
  - (a) adding the ethylenically unsaturated functionalized organic compound to the homogeneous ethylene polymer to  
10 form a branched homogeneous polymer, and thereafter
  - (b) reacting the reactive thermoplastic polymer with the branched homogeneous ethylene polymer to form a branched block ethylene polymer; and thereafter
- (2) blending the branched block ethylene polymer with the  
15 thermoplastic blending or molding polymer.

In one preferred aspect, the reactive thermoplastic polymer of component (c) will be an amine-functionalized polymer. In another preferred aspect, the reactive thermoplastic polymer of component (c)  
20 will be a polyester.

Surprisingly articles molded from the compositions of this invention show advantageous temperature storage modulus in excess of that exhibited by either a blend of corresponding polymers described  
25 in (a) and (c) [hereinafter (a)/(c)] or polymer (a) grafted only with (b) [hereinafter (a)/(b)]. That is, the branched block ethylene polymers of the invention soften and deform at higher temperatures, i.e. they exhibit a greater upper service temperature than (a)/(c) blends or (a)/(b) grafts. Also the branched block ethylene polymers  
30 of the invention show a surprisingly lower Tan Delta than that of the (a)/(b) grafts or (a)/(c) blends.

Figures 1-18 are graphs (charts). Figure 1 shows the storage modulus of a branched block ethylene polymer of the invention  
35 (designated +++) compared with controls which are not examples of the invention. Figures 2a and 2b are DMS Rheology Comparisons of branched

- (c) a reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated organic compound.

In a preferred embodiment, this invention involves a composition comprising a blend of a thermoplastic blending or molding polymer with a branched block ethylene polymer, wherein the branched block ethylene polymer comprises

- (a) a homogeneous ethylene polymer which has:
- (i) a  $M_w/M_n$  ratio, as determined by gel permeation chromatography, of less than about 3.0;
  - (ii) a density of about 0.93 g/cm<sup>3</sup> or less; and
  - (iii) a Short Chain Branching Distribution Index of greater than about thirty percent;
- (b) an ethylenically unsaturated organic compound; and
- (c) a reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated organic compound.

In yet another aspect, this invention involves a method of preparing a composition from a thermoplastic blending or molding polymer, an ethylene polymer, an ethylenically unsaturated functionalized organic compound; and a reactive thermoplastic polymer, said method comprising:

- (1) forming a branched block ethylene polymer by
- (a) adding the ethylenically unsaturated functionalized organic compound to the ethylene polymer to form a branched ethylene polymer, and thereafter
  - (b) reacting the reactive thermoplastic polymer with the branched ethylene polymer to form a branched block ethylene polymer; and thereafter
- (2) blending the branched block ethylene polymer with the thermoplastic blending or molding polymer.

In a preferred aspect, this invention involves a method of preparing a composition from a thermoplastic blending or molding polymer; a homogeneous ethylene polymer which has a  $M_w/M_n$  ratio, as



shows how the melt strength is improved by the addition of various percentages of Nylon 6 to MAHg8200. Figure 15 shows the effect of oil on viscosity of branched block ethylene polymers which comprise Nylon 6 grafted via maleic anhydride to a homogeneous ethylene polymer represented by XU58300, an ethylene polymer available from The Dow Chemical Company. Figure 16 shows the effect of oil on tan delta of branched block ethylene polymers which comprise Nylon 6 grafted via maleic anhydride to a homogeneous ethylene polymer represented by XU58300, an ethylene polymer available from The Dow Chemical Company. Figure 17 compares various branched block ethylene polymers which comprise various reactive thermoplastic polymers, i.e., PPO/HIPS (polyphenylene oxide/high impact polystyrene), PCTG, PET and Nylon 6, grafted via maleic anhydride to MAHg8200. Figure 18 shows the shore A hardness at various temperatures, as achieved by branched block ethylene polymers which comprise 70 weight percent MAHg8200 and 30 weight percent Nylon 6.

Figure 19 is a plot of viscosity in relation to frequency of rotation determined by rheometric (dynamic) mechanical spectroscopy at 230°C for compositions containing by weight 75% polypropylene and 0, 10, 15, 20, 25 and 30% branched block ethylene polymer.

Figure 20 is a plot of tan delta in relation to frequency of rotation determined by rheometric (dynamic) mechanical spectroscopy at 230°C for compositions containing by weight 75% polypropylene and 0, 10, 15, 20, 25 and 30% branched block ethylene polymer.

In the Figures ITP is a substantially linear ethylene polymer; PBT is polybutyleneterephthalate; MAH is maleic anhydride; MMA/GMS is methacrylate-butylacrylate-glycidyl methacrylate, 98:8:2 ratio by weight as further explained in the examples of the invention. DMS is dynamic mechanical spectrometry; RMS is rheolometric mechanical spectrometry. The acronym POE is also used for polyolefin elastomer in the figures for the homogeneous ethylene polymer. RSA is Rheometrics Solids Analyzer

block ethylene polymers of the invention designated with triangles compared with controls which are not examples of the invention.

Figure 3 shows the tan delta, E' and E'' of a branched block ethylene polymer of the invention. Figure 4 shows the RMS rheology data at 190

5 ° C of a branched block ethylene polymer of the invention designated by diamonds compared with controls which are not examples of the invention. Figure 5 shows the tan delta at 190° C of a branched block ethylene polymer of the invention designated by diamonds compared with controls which are not examples of the invention. Figure 6 shows the  
10 RMS Rheology data at 190° C of branched block ethylene polymers of the invention having different ratios of homogeneous ethylene polymer grafted to maleic anhydride to a reactive thermoplastic polymer represented by nylon. Figure 7 shows the RMS Rheology data at 230° C of branched block ethylene polymers of the invention having different  
15 ratios of homogeneous ethylene polymer grafted to maleic anhydride to a reactive thermoplastic polymer represented by nylon. Figure 8 shows the tan delta at 190° C of branched block ethylene polymers of the invention having different ratios of homogeneous ethylene polymer grafted to maleic anhydride to a reactive thermoplastic polymer  
20 represented by nylon. Figure 9 shows the tan delta at 230° C of branched block ethylene polymers of the invention having different ratios of homogeneous ethylene polymer grafted to maleic anhydride to a reactive thermoplastic polymer represented by nylon.

25 Figure 10 compares the RMS data at 190° C for a homogeneous ethylene polymer grafted with maleic anhydride (designated MAHg8200 where 8200 is the designation of the ethylene polymer, Engage™ 8200) (not an example of the invention) with branched block ethylene  
30 polymers formed by reacting that grafted polymer with PCTG (poly cyclohexanoldimethol terephthalate glycol), PET (polyethylene terephthalate) and Nylon 6. Figure 11 shows the RMS data at 190° C of MAHg8200 (as described above) with branched block ethylene polymers formed by reacting that grafted polymer with Nylon 6, Nylon 11, and  
35 Nylon 12. Figure 12 shows the same comparison as Figure 11, but at 230° C. Figure 13 shows how the rheology index is improved by the addition of various percentages of Nylon 6 to MAHg8200. Figure 14

reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated functionalized organic compound. The ethylene polymer may be considered to be a first polymer block. The ethylenically unsaturated functionalized organic compound adds to the ethylene polymer through its double bond to form a branched ethylene polymer. If the branch formed by the ethylenically unsaturated functionalized organic compound is of sufficient length (containing, for example, three or more molecules), it may be said to form a second block itself. However, the branch may be formed by just a single molecule of the ethylenically unsaturated functionalized organic compound. Regardless of the length of the branch formed by the ethylenically unsaturated functionalized organic compound, the branched ethylene polymer reacts, through the functionality on the residue of the ethylenically unsaturated functionalized organic compound, with the reactive thermoplastic polymer, to form the final polymer block.

The branch point, which contains the residue of one or more molecules of the ethylenically unsaturated functionalized organic compound and allows the bonding of the reactive thermoplastic polymer as the final polymer block, may be distinguished from long- and short-chain branching which may occur on an ethylene polymer during its formation from ethylene and (optionally) another monomer(s) such as an alpha-olefin. The branch point formed from an ethylenically unsaturated functionalized organic compound, in contrast to branches formed in conjunction with backbone growth during the polymerization of ethylene, is added to an ethylene polymer after its original polymerization to provide the necessary reactive site for bonding of the reactive thermoplastic polymer as the final polymer block of the branched block ethylene polymer.

#### Concerning Subcomponent (a) - The Ethylene Polymer

Subcomponent (a) is an ethylene polymer which forms the first block in the preparation of the branched block ethylene polymers of the invention. An ethylene polymer useful for such purpose may include, among others, conventional ethylene polymers

The compositions of this invention are useful, in any application for which impact modified polymers are used. For example, they are useful in the production of films, fibers, coatings, extruded sheets, multi-layer laminates and molded or shaped articles of  
5 virtually all varieties, especially profile extruded gaskets, blow molded or thermoformed articles, automotive fascia, body side moldings and interior components, and other parts and components for use in the automotive, electrical and electronics industries. The compositions  
10 of this invention are also useful as hot melt adhesives. The methods of this invention are useful for preparing polymers, compositions and molded articles having applications which are the same as or similar to the foregoing.

Branched block ethylene polymers of the invention are  
15 surprisingly useful as rheologic modifiers, impact strength modifiers and melt strength enhancers. Modifier effectiveness is a function of melt elasticity, dispersibility and compatibility of the branched block ethylene polymer. The branched block ethylene polymers are useful in blow molding and thermoforming. They are also  
20 advantageously useful in oil extension. Additionally, especially when the reactive thermoplastic polymer is an amine-functionalized polymer, such as nylon, the branched block ethylene polymer is useful in forming non-crosslinked foams which are recyclable. In the case of branched block ethylene polymers wherein the reactive thermoplastic  
25 polymer is a nylon, branched block ethylene polymers which utilize Nylon 11 as the reactive thermoplastic polymer offer the highest melt strength, followed by that utilizing Nylon 6, followed by that utilizing Nylon 12.

### 30 Detailed Description of the Invention

The branched block ethylene polymers of this invention, are prepared from (i) an ethylene polymer, preferably a polymer having an  $M_w/M_n$  ratio as defined by gel permeation chromatography of less than  
35 about 3.0, and more preferably a homogeneous ethylene polymer; (ii) an ethylenically unsaturated functionalized organic compound; and (iii) a

pressure conditions. LLDPE can be formed as a slurry in a light hydrocarbon diluent using a supported chromium catalyst, or it can be formed as a slurry in hexane using organometal-titanium type catalysts. It can also be formed in a suitable hydrocarbon in solution at approximately 250°C, or it can be formed in gas phase as described in Levine, USP 4,011,382, or as described in Jezl, USP 4,129,729.

HDPE homopolymer or copolymers are typically about 94% crystalline and have densities of above about 0.935 g/cm<sup>3</sup>, and particularly from about 0.950 to about 0.970 g/cm<sup>3</sup>. HDPE, because of its much greater crystallinity and density, has a higher melting point than LDPE - 135°C vs. 115°C. A crystalline HDPE homopolymer has a regular linearity, and typically forms as it cools into ordered agglomerates referred to as crystallites, from which HDPE obtains an excellent degree of toughness and shatter-resistant character. Crystallization is disturbed, and density is correspondingly decreased in HDPE, if ethylene is copolymerized with an  $\alpha$ -olefin, as described above, or if short-chain branching results from side reactions intrinsic for a particular reaction mechanism. For example, HDPE prepared with Ziegler transition metal catalysts may have from about 0.5 to 4 short-chain branches, particularly methyl groups, per 1000 carbon atoms. The molecular weight of HDPE usually ranges from 50,000 to 1,000,000 or more. Beyond a certain point, increasing the molecular weight of HDPE actually causes a decrease in density because of chain entanglement, but the effect is not significant. Most aspects of the strength of HDPE decrease with decreasing molecular weight. HDPE may be manufactured in a slurry system wherein high purity ethylene is fed to a loop reactor which contains a low boiling hydrocarbon used to dissolve the ethylene, and to suspend the catalyst and polymer particles. Alternatively, HDPE can be made in a gas-phase process wherein no hydrocarbon diluent is used and a fluidized bed is used to agitate and suspend the polymer particles. Methods for making HDPE are more particularly described in Hogan, USP 2,825,721.

Concerning the Use of a Homogeneous Ethylene Polymer as Subcomponent (a). Preferably, subcomponent (a) will be a homogeneous

such as low density polyethylene ("LDPE"), linear low density polyethylene ("LLDPE"), and high density polyethylene ("HDPE"). LDPE is typically thought of as that which is made under high pressure conditions and has a density from about 0.915 to about 0.935 g/cm<sup>3</sup>. This low density results from the many zones of amorphous arrangement which are characteristic of LDPE because of its long-chain branches, many of which are as long as the backbone. Inasmuch as the density of purely amorphous polyethylene is 0.855 g/cm<sup>3</sup>, as compared to purely crystalline polyethylene which has a density of 0.97 g/cm<sup>3</sup>, it can be seen that LDPE does have some crystallinity. However its long-chain branching is its dominant feature. LDPE typically has from 4 to 25 and sometimes as many as 90 of such long-chain branches per 1000 carbon atoms. It also has 10-35 short chains per 1000 carbon atoms, containing 2-8 carbon atoms each, which result from backbiting and molecular rearrangement along the backbone during chain growth, rather than from comonomer incorporation as is the case for LLDPE.

LDPE can be made in either a tubular reactor or a stirred autoclave, where heated, pressurized feed streams of ethylene gas, free-radical initiator and optional chain transfer agent are injected into the reaction device. The reaction of formation usually occurs at 1,500-3,000 atm (152-304 MPa) and at a temperature usually not exceeding 300°C, as known in the art. During the polymerization of LDPE, ethylene can be copolymerized with other monomers such as vinyl acetate, ethyl acrylate, acrylic acid, vinyl chloride or carbon monoxide.

LLDPE is formed under the kind of low pressure conditions which are usually thought of as appropriate for forming HDPE. However, a low density product (0.910 - 0.940 g/cm<sup>3</sup>) results because, rather than forming a homopolymer, ethylene is copolymerized with one or more  $\alpha$ -olefins, which in the final product take on the form and function of short side chains. Because the comonomers most frequently used are  $\alpha$ -olefins such as 1-butene, 4-methyl-1-pentene, 1-hexene or 1-octene, these side chains prevent the close, fully crystalline type of packing representative of HDPE, but they are not nearly as long as the fully branched, long side chains associated with LDPE made under high

The polydispersity ( $M_w/M_n$ ) for the homogeneous ethylene polymers described herein is less than about 3.0, is preferably from about 1.5 to about 2.5, and is more preferably from about 1.7 to about 2.3, and is most preferably about 2.

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When they are an ethylene/ $\alpha$ -olefin interpolymer, the homogeneous ethylene polymers will have a homogeneous branching distribution. The terms "homogeneously branched" and "homogeneous branching distribution" refer to the fact that (1) the  $\alpha$ -olefin comonomer(s) is/are randomly distributed within a given molecule of an ethylene/comonomer copolymer; (2) substantially all of the copolymer molecules have the same ethylene/comonomer ratio; (3) the polymer is characterized by a narrow short chain branching distribution; (4) the polymer essentially lacks a measurable high density, crystalline polymer fraction [as measured, for example, by techniques such as those involving polymer fractional elutions as a function of temperature]; and (5) the polymer is characterized, as determined from the conditions described in 21 C.F.R. 177.1520(c) and (d), as having (i) substantially reduced levels of n-hexane extractables (for example, less than 1% extractables for an ethylene/1-octene copolymer at densities greater than about 0.90 g/cc), or (ii) substantial amorphism, which is indicated when greater than 75 wt% of the polymer is soluble under the specified conditions (for example, ethylene/1-octene copolymer is 90% soluble at a density of about 0.90 g/cm<sup>3</sup>, and is 100% is soluble at a density of about 0.88 g/cm<sup>3</sup>).

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Typically, the homogeneous ethylene polymers have a homogeneous short chain branching distribution and do not have any measurable high density fraction, i.e., these polymers do not contain any polymer fraction that has a degree of branching less than or equal to 2 methyls/1000 carbons, as measured by Temperature Rising Elution Fractionation which is described in USP 5,089,321.

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The homogeneity or narrowness of the branching distribution is further indicated by the value of the Composition Distribution Branch Index ("CDBI") or the Short Chain Branch Distribution Index ("SCBDI").

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ethylene polymer. Homogeneous polymers are characterized as having a narrow polydispersity ( $M_w/M_n$ ) and a homogeneous short chain branching distribution. The polydispersity ( $M_w/M_n$ ) of the homogeneous ethylene polymers described herein may be determined from data generated by gel permeation chromatography (GPC). An instrument typically used for this purpose is a Waters 150°C high temperature chromatographic unit equipped with three mixed porosity bed columns (Polymer Laboratories 103, 104, 105 and 106), operating at a system temperature of 140°C. The solvent used is 1,2,4-trichlorobenzene, from which 0.3 weight percent solutions of the samples are prepared for injection. The flow rate is 1.0 milliliter/minute, and the injection size is 200 microliters.

Molecular weight determination for polyethylene is made by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene, as described by Williams and Word in *Journal of Polymer Science, Polymer Letters*, volume 6, page 621, 1968 (incorporated herein by reference), to derive the following equation:

$$M_{\text{polyethylene}} = a * (M_{\text{polystyrene}})^b$$

in which  $a = 0.4316$ ,  $b = 1.0$ , and  $M$  is molecular weight for polyethylene and polystyrene in 1,2,4-trichlorobenzene. Weight average molecular weight,  $M_w$ , is calculated in the usual manner according to the following formula:  $M_w = \sum w_i * M_i$ , where  $w_i$  and  $M_i$  are the weight fraction and molecular weight, respectively, of the  $i^{\text{th}}$  fraction eluting from the GPC column. Number average molecular weight,  $M_n$ , is calculated in the usual manner according to the following formula:  $M_n = [\sum n_i * M_i] / \sum n_i$ , where  $n_i$  and  $M_i$  are, respectively, the number of molecules in, and the molecular weight of, the  $i^{\text{th}}$  fraction eluting from the GPC column. The symbol  $*$  indicates a step of multiplication.



27°C, and more typically within 20°C of the melting point of the single melting peak.

The single melting peak is determined using a differential scanning calorimeter standardized with indium and deionized water. The method involves about 5 samples of 7 mg size, a "first heat" to about 150°C which is held for 4 minutes, a cool down at 10°C/min to 30°C which is held for 3 minutes, and a heat up at 10°C/min to 150°C for the "second heat" heat flow versus temperature curve. Total heat of fusion of the polymer is calculated from the area under the curve. The heat of fusion attributable to the artifact described above, if present, can be determined using an analytical balance and weight percent calculations.

One known class of homogeneous ethylene polymers are "homogeneous linear ethylene polymers." Homogeneous ethylene polymers have no long-chain branching, as defined below. The term "linear" does not refer to bulk high pressure branched polyethylene, ethylene/vinyl acetate copolymers, or ethylene/vinyl alcohol copolymers inasmuch as these kinds of polymers are known to those skilled in the art to have numerous long chain branches.

Homogeneous linear ethylene polymers are from a known class of polymers, examples of which include those described in USP 3,645,992 (Elston), those made using so called single site catalysts in a batch reactor having relatively high ethylene concentrations [as described in U.S. Patent 5,026,798 (Canich) or in U.S. Patent 5,055,438 (Canich)], and those made using constrained geometry catalysts in a batch reactor also having relatively high olefin concentrations [as described in U.S. Patent 5,064,802 (Stevens) or in EP-A-416 815 (Stevens)]. These polymers have an absence of long chain branching, as described by Van der Sanden and Halle in *Tappi Journal*, February 1992. Processes using metallocene catalysts to produce homogeneous linear ethylene polymers have been developed, as shown, for example, in Ewen, USP 4,937,299, EP 129,368, EP 260,999, USP 4,701,432, USP 4,937,301, USP 4,935,397, USP 5,055,438 and WO 90/07526, each of which

CDBI is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated, for example, by employing temperature rising elution fractionation, as  
5 described in Wild, *Journal of Polymer Science, Polymer Physics* Edition, Volume 20, page 441 (1982), or in U.S. Patent 4,798,081. The CDBI for the homogeneous ethylene/ $\alpha$ -olefin interpolymers used in the present invention is greater than about 30 percent, is preferably greater than about 50 percent, is more preferably greater than about  
10 80 percent, and is most preferably greater than about 90 percent.

Homogeneous ethylene polymers do not include, by definition, heterogeneously branched linear low density polyethylenes or linear high density polyethylenes made using Ziegler-Natta polymerization  
15 processes (as described, for example, in Anderson, USP 4,076,698); or the branched high pressure, free-radical polyethylenes and other high pressure ethylene copolymers (e.g., ethylene/vinyl acetate or ethylene/vinyl alcohol copolymers), which are known to those skilled in the art to have numerous long chain branches.

20

To the extent that the homogeneous ethylene polymer in an ethylene/ $\alpha$ -olefin interpolymers, it will have only a single melting peak, as measured by differential scanning calorimetry (DSC) between -30°C and 150°C. This is in contrast to Ziegler-polymerized,  
25 heterogeneously branched linear ethylene polymers, which have 2 or more melting peaks because of their broad branching distribution. However, for certain classes of homogeneous ethylene polymers having a density of about 0.875 g/cm<sup>3</sup> and about 0.91 g/cm<sup>3</sup>, the single melt peak may show, depending on equipment sensitivity, a "shoulder" or a  
30 "hump" on the low side of the melting peak (i.e. below the melting point) that constitutes less than 12 percent, typically, less than 9 percent, more typically less than 6 percent of the total heat of fusion of the polymer. This artifact is due to intrapolymer chain variations, and it is discerned on the basis of the slope of the  
35 single melting peak varying monotonically through the melting region of the artifact. Such artifact occurs within 34°C, typically within

herein, the onset of surface melt fracture is characterized as the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40x magnification. Substantially linear ethylene polymers will further be characterized by a critical shear rate at the onset of surface melt fracture which is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same  $I_2$  and  $M_w/M_n$ . An apparent shear stress versus apparent shear rate plot is used to identify the melt fracture phenomena over a range of nitrogen pressures from 5250 to 500 psig using the die or gas extrusion rheometer (GER) test apparatus as described by Shida et al in *Polymer Engineering Science*, Volume 17, No. 11 (1977), page 770, and in *Rheometers for Molten Plastics* by John Dealy, Van Nostrand Reinhold Co. (1982), pages 97-99. According to Ramamurthy in *Journal of Rheology*, 30(2), 337-357 (1986), above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions, and ranges in detail from loss of specular gloss to the more severe form of "sharkskin". In this disclosure, the onset of surface melt fracture is characterized as the beginning of the loss of extrudate gloss, at which the surface roughness of extrudate can only be detected by 40X magnification. The critical shear rate at onset of surface melt fracture for a substantially linear ethylene polymer is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture for a conventional linear ethylene polymer as to which the  $I_2$ , polydispersity and density is each within 90-110 percent of the corresponding value for the substantially linear ethylene polymer. Preferably, the critical shear stress at the onset of surface melt fracture for the substantially linear ethylene polymers is greater than about  $2.8 \times 10^6$  dynes/cm<sup>2</sup>.

Gross melt fracture occurs at unsteady flow conditions, and ranges in detail from regular surface distortions (such as alternating roughness and smoothness, or helical patterns) to random distortions.

is incorporated herein by reference. Such polymers can be made by conventional polymerization processes such as gas phase, slurry or solution.

5 A preferred, known class of homogeneous ethylene polymers are "substantially linear ethylene polymers", and are characterized by a desirable level of processability, e.g. low susceptibility to melt fracture, even under high shear stress conditions. Substantially linear ethylene polymers have a critical shear rate at the onset of  
10 surface melt fracture which is substantially higher than, and a processing index which is substantially lower than, that of a linear polyethylene at the same molecular weight distribution and melt index. Substantially linear ethylene polymers have a shear thinning and ease of processability similar to highly branched low density polyethylene  
15 (LDPE), but also have the strength and toughness of linear low density polyethylene (LLDPE). The substantially linear ethylene polymers described herein, and processes for making same, are also described in USP 5,272,236, USP 5,278,272 and U.S. SN 08/301,948.

20 As used herein, "substantially linear ethylene polymer" means that, in addition to the short chain branches attributable to any comonomer incorporation, the polymer is further characterized as having long chain branches. Substantially linear ethylene polymers are characterized as having a melt flow ratio  $I_{10}/I_2$  which is greater  
25 than or equal to 5.63, a molecular weight distribution (as determined by gel permeation chromatography)  $M_w/M_n$  which is less than or equal to  $I_{10}/I_2 - 4.63$ , and a critical shear rate at the onset of surface melt fracture at least 50 percent greater than a linear ethylene polymer having essentially the same  $I_2$  and  $M_w/M_n$  and/or a critical shear stress  
30 at the onset of surface melt fracture of greater than about  $2.8 \times 10^5$  dynes/cm<sup>2</sup>.

According to Ramamurthy in *Journal of Rheology*, 30(2), 337-357, 1986, above a certain critical flow rate, surface melt fracture may  
35 occur, which may result in irregularities ranging from loss of specular gloss to the more severe form of "sharkskin". As used

where  $2.15 \times 10^6$  dyne/cm<sup>2</sup> is the shear stress at 2500 psi, and the shear rate is the shear rate at the wall as represented by the following equation:

$$\frac{32Q'}{(60 \text{ sec/min})(0.745)(\text{diameter} \times 2.54 \text{ cm/in})^3}$$

where:  $Q'$  is the extrusion rate in g/min, 0.745 is the melt density of polyethylene in g/cm<sup>3</sup>, and diameter is the orifice diameter of the capillary in inches. The  $PI$  is the apparent viscosity of a material measured at an apparent shear stress of  $2.15 \times 10^6$  dynes/cm<sup>2</sup>.

For a substantially linear ethylene polymer, the  $PI$  is less than or equal to 70 percent of that of a conventional linear ethylene polymer as to which the  $I_2$ ,  $M_w/M_n$  and density is each within 90-110 percent of the corresponding value for the substantially linear ethylene polymer.

Substantially linear ethylene polymers further have an improved melt elasticity or melt tension as compared to homogeneous linear ethylene polymers. "Melt tension" is measured by a specially designed pulley transducer in conjunction with a melt indexer. Melt tension is the load exerted by the extrudate or filament while passing over the pulley onto a two inch drum rotating at the standard speed of 30 rpm. The melt tension measurement is similar to that performed by the "Melt Tension Tester" made by Toyoseiki, and is described by John Dealy in *Rheometers for Molten Plastics*, Van Nostrand Reinhold Co. (1982), pages 250-251. The melt tension of the substantially linear ethylene polymers described herein is at least about 2 grams, and, particularly with respect to those having a narrow molecular weight distribution such as about 1.5 to 2.5, the melt tension is typically at least about 5 percent, and can be as much as about 60 percent, greater than the melt tension of a conventional linear ethylene interpolymers as to which the melt index, polydispersity and density is each within 90-110 percent of the corresponding value for the substantially linear ethylene polymer.

For commercial acceptability (e.g. in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF), and the critical shear stress at onset of gross melt fracture (OGMF), are related herein to the changes of surface roughness and configurations of the extrudate produced by a GER. For the substantially linear ethylene polymers described herein, the critical shear stress at onset of gross melt fracture is preferably greater than about  $4 \times 10^6$  dyne/cm<sup>2</sup>.

For the GER melt fracture determination and for the processing index (PI) determination described below, the substantially linear ethylene polymers are tested without inorganic fillers, and with 20 ppm or less aluminum catalyst residue. For these determinations the polymer will preferably contain, antioxidants, such as phenols, hindered phenols, phosphites or phosphonites, preferably a combination of a phenol or hindered phenol and a phosphite or a phosphonite.

A further indicator of the improved processability of substantially linear ethylene polymers is the rheological processing index (PI). The PI is the apparent viscosity (in kpoise) of a polymer, and is measured by a gas extrusion rheometer (GER). The GER is described above in conjunction with the determination of melt fracture phenomena. The processing index is measured at 190°C with a nitrogen pressure of 2500 psig. For high flow polymers (e.g. polymer having an I<sub>2</sub> of 50 - 100 g/10 min. or greater), a die having a diameter of 0.0296 inch (752 microns), preferably 0.0143 inch, having a 20:1 length/diameter ratio, and having an entrance angle of 180° is used.

The processing index is calculated in millipoise units from the following equation:

$$PI = \frac{2.15 \times 10^6 \text{ dyne/cm}^2}{(1000 \times \text{shear rate})}$$

polymerization process, although slurry and gas phase polymerization processes are also useful, provided the proper catalysts and polymerization conditions are employed. Multiple reactor polymerization processes are also useful for this purpose, such as  
5 those disclosed in USP 3,914,342. The multiple reactors can be operated in series or in parallel, with at least one constrained geometry catalyst employed in at least one of the reactors.

In general, continuous polymerization is advantageously  
10 accomplished at conditions known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, for example, temperatures from about 0 to 250°C and pressures from atmospheric to 1000 atmospheres (100 MPa). A support may be employed, but preferably the catalysts are used in a homogeneous (i.e. soluble) manner. It will,  
15 of course, be appreciated that the active catalyst system forms in situ if the catalyst, and the cocatalyst components thereof, are added directly to the polymerization process, and a suitable solvent or diluent, including condensed monomer, is used. It is, however, preferred to form the active catalyst in a separate step in a suitable  
20 solvent prior to adding same to the polymerization mixture.

Preferably, the term "substantially linear ethylene polymer" designates that the bulk polymer is substituted, on average, with about 0.01 long-chain branch/1000 total carbon atoms (including both  
25 backbone and branch carbons) to about 3 long-chain branches/1000 total carbons. Preferred polymers are substituted with about 0.01 long-chain branch/1000 total carbons to about 1 long-chain branch/1000 total carbons, more preferably from about 0.05 long-chain branch/1000 total carbons to about 1 long-chain branch/1000 total carbons, and  
30 especially from about 0.3 long-chain branch/1000 total carbons to about 1 long-chain branch/1000 total carbons.

As used herein, the term "backbone" refers to a discrete molecule, and the term "polymer" or "bulk polymer" refers in the  
35 conventional sense to the polymer as formed in a reactor. The term "bulk" polymer means the polymer which results from the polymerization

A further unique characteristic of these substantially linear ethylene polymers is a flow property which causes the  $I_{10}/I_2$  value to be essentially independent of polydispersity ( $M_w/M_n$ ). This is a significant difference from conventional Ziegler-polymerized heterogeneous polyethylene resins, and from conventional single-site-catalyst-polymerized homogeneous polyethylene resins, the rheological properties of which are such that as polydispersity ( $M_w/M_n$ ) increases, the  $I_{10}/I_2$  value also increases. It should be noted that peroxide need not be added to the substantially linear ethylene polymers in order for the polymers to exhibit an  $I_{10}/I_2$  independent of polydispersity ( $M_w/M_n$ ) and the melt fracture properties.

Generally, the  $I_{10}/I_2$  ratio of the substantially linear ethylene polymers is at least about 5.63, is preferably at least about 7, is especially at least about 8, and is most preferably at least about 9 or above. The only limitation on the maximum  $I_{10}/I_2$  ratio are practical considerations such as economics or polymerization kinetics, but typically the maximum  $I_{10}/I_2$  ratio does not exceed about 20, and preferably does not exceed about 15. In contrast, the  $I_{10}/I_2$  ratio of the homogeneous linear ethylene polymers described herein is generally 6 or less.

The advantageous melt elasticity and processibility of substantially linear ethylene polymers result, it is believed, from their method of production. The polymers may be produced via a continuous (as opposed to a batch) controlled polymerization process using at least one reactor, for example as disclosed in WO 93/07187, WO 93/07188 or WO 93/07189. However, these polymers can also be produced using multiple reactors, using for example a multiple reactor configuration as described in USP 3,914,342 at a polymerization temperature and pressure sufficient to produce the interpolymers having the desired properties.

The polymerization conditions for manufacturing substantially linear ethylene polymers are generally those useful in a solution



Long-chain branching can be distinguished from short-chain branching by using  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy (NMR), and, for ethylene homopolymers and for copolymers of ethylene and a  $\text{C}_2\text{-C}_6$   $\alpha$ -olefin, it can be quantified using the method of Randall in  
5 *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics*, Volume C29, pages 285-297 (1989). However, as a practical matter, the portion of a long-chain branch beyond the sixth carbon atom cannot be distinguished using current  $^{13}\text{C}$  NMR for the purpose of determining the precise length of the long-chain branch  
10 and, as such, this analytical technique cannot distinguish between a seven (7) carbon branch and a seventy (70) carbon branch.

USP 4,500,648, incorporated herein by reference, teaches that long-chain branching frequency (LCBF) can be represented by the  
15 equation  $\text{LCBF} = b/\text{Mw}$  where  $b$  is the weight average number of long-chain branches per molecule, and  $\text{Mw}$  is the weight average molecular weight. The molecular weight averages and the long-chain branching characteristics are determined by gel permeation chromatography and intrinsic viscosity methods.

20 Other known techniques useful for determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers. Two such methods are gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS)  
25 and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV). The use of these techniques for long chain branch detection and the underlying theories have been well documented in the literature. See, e.g., Zimm, G.H. and Stockmayer, W.H., *J. Chem. Phys.*, 17, 1301 (1949) and Rudin, A., *Modern Methods of*  
30 *Polymer Characterization*, John Wiley & Sons, New York (1991) pp. 103-112.

A. Willem deGroot and P. Steve Chum, both of The Dow Chemical Company, at the October 4, 1994 conference of the Federation of  
35 Analytical Chemistry and Spectroscopy Society (FACSS) in St. Louis, Missouri, presented data demonstrating that GPC-DV is a useful

process and, for these substantially linear ethylene polymers, includes molecules having both an absence of long-chain branching, as well as molecules which do have long-chain branching. Thus a "bulk" polymer includes all molecules formed during polymerization. It is understood that, for the substantially linear ethylene polymers, not all molecules have long-chain branching, but a sufficient number of same do such that the average long-chain branching content of the bulk polymer advantageously affects the melt rheology (i.e. the melt fracture properties) of the bulk polymer. For the polymer to be a "substantially linear" ethylene polymer, the polymer must have at least enough molecules with long-chain branching such that the average long-chain branching in the bulk polymer is at least an average of about 0.01/1000 total carbons.

When a substantially linear ethylene polymer, which contains long-chain branching, is an ethylene/ $\alpha$ -olefin interpolymers, the long-chain branch may have a chain length of at least one (1) carbon less than the number of carbons in the comonomer. A short-chain branch, by contrast, is defined as having a chain length of the same number of carbons in the residue of the comonomer after it is incorporated into the polymer molecule backbone. For example, an ethylene/1-octene substantially linear ethylene polymer has a backbone with long-chain branches of at least seven (7) carbons in length, but it also has short chain branches of only six (6) carbons in length.

For ethylene/ $\alpha$ -olefin interpolymers, the long chain branch is longer than the short chain branch that results from the incorporation of the  $\alpha$ -olefin(s) into the polymer backbone. The empirical effect of the presence of long chain branching in the substantial linear ethylene/ $\alpha$ -olefin interpolymers used in the invention is manifested as enhanced rheological properties which are quantified and expressed herein in terms of gas extrusion rheometry (GER) results and/or melt flow,  $I_{10}/I_2$ , increases, as is described above.

"Substantially linear ethylene polymers" are prepared by using constrained geometry catalysts, and are characterized by a narrow polydispersity (molecular weight distribution) and by a narrow comonomer distribution. As herein used, "interpolymer" means a polymer of two or more comonomers, e.g., a copolymer, terpolymer, etc., or in other words, a polymer made by polymerizing ethylene with at least one other comonomer. Other basic characteristics of these substantially linear ethylene polymers include a low residuals content (i.e., low concentrations in the substantially linear ethylene polymer of the catalyst used to prepare the polymer, unreacted comonomers, and low molecular weight oligomers made during the course of the polymerization), and a controlled molecular architecture which provides good processability even though the molecular weight distribution is narrow relative to conventional olefin polymers.

Although it is preferred to use a substantially linear ethylene polymer for preparation of the branched block ethylene polymers, a combination of any two or more of the different kinds of ethylene polymers described above may be used as well. The differences in the various kinds of ethylene polymers may be illustrated by the use, for example, of (i) a conventional LLDPE together with a substantially linear ethylene polymer, or (ii) a substantially linear ethylene homopolymer together with a substantially linear ethylene/ $\alpha$ -olefin interpolymer, (iii) two or more substantially linear ethylene polymers made with different constrained geometry catalysts, (iv) two or more substantially linear ethylene polymers made in different reactors or reaction zones, or (v) two or more substantially linear ethylene polymers having different properties such as density,  $M_w/M_n$ ,  $I_2$  or  $I_{10}/I_2$ . The differences among the ethylene polymers contained in such a combination may manifest themselves in the form, for example, of multi-modal densities, a broadened  $M_w/M_n$ , and/or multiple melting peaks. Such a combination of ethylene polymers, if employed, may be advantageously prepared using the dual reaction polymerization process described below.

#### General Properties of the Ethylene Polymer:

technique for quantifying the presence of long chain branches in substantially linear ethylene interpolymers. In particular, deGroot and Chum found that the level of long chain branches in substantially linear ethylene homopolymer samples measured using the Zimm-Stockmayer equation correlated well with the level of long chain branches measured using  $^{13}\text{C}$  NMR.

Further, deGroot and Chum found that the presence of octene does not change the hydrodynamic volume of the polyethylene samples in solution and, as such, one can account for the molecular weight increase attributable to octene short chain branches by knowing the mole percent octene in the sample. By deconvoluting the contribution to molecular weight increase attributable to 1-octene short chain branches, deGroot and Chum showed that GPC-DV may be used to quantify the level of long chain branches in substantially linear ethylene/octene copolymers.

deGroot and Chum also showed that a plot of  $\text{Log}(I_2, \text{Melt Index})$  as a function of  $\text{Log}(\text{GPC Weight Average Molecular Weight})$  as determined by GPC-DV illustrates that the long chain branching aspects (but not the extent of long branching) of substantially linear ethylene polymers are comparable to that of high pressure, highly branched low density polyethylene (LDPE) and are clearly distinct from ethylene polymers produced using Ziegler-type catalysts such as titanium complexes and ordinary homogeneous catalysts such as hafnium and vanadium complexes.

In contrast to the term "substantially linear ethylene polymer", the term "linear" means that the polymer lacks measurable or demonstrable long chain branches, i.e., the polymer is substituted with an average of less than 0.01 long branch/1000 carbons, with long chain branching being defined herein as a chain length of at least 6 carbons, above which the length cannot be distinguished using  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy.

The molecular weight of the ethylene polymer is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg [formerly known as "Condition (E)" and also known as I<sub>2</sub>]. Melt index value is

5 inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The I<sub>2</sub> melt index for the ethylene polymer will be generally about 0.01 grams/10 minutes ("g/10 min") or more, preferably about 0.1 g/10 min or more, more

10 preferably about 0.5 g/10 min or more, and most preferably about 1.0 g/10 min or more. The I<sub>2</sub> melt index for the ethylene polymer will be generally about 1000 g/10 min or less, preferably about 500 g/10 min or less, more preferably about 250 g/10 min or less, and most preferably about 100 g/10 min or less.

15

The Use of Dual Reactor Systems to Prepare the Ethylene Polymer:

Multiple reactor polymerization processes, such as those disclosed in USP 3,914,342, U.S. SN 08/010,958 (filed January 29, 1993) and U.S. SN 08/208,068 (filed March 8, 1994), in which the multiple reactors can

20 be operated in series or in parallel, are often advantageous in preparing ethylene polymers. When the reactors are run in parallel, the polymerization product of each, while still in solution, is combined together in one mixture. When multiple reactors are run in series, the product of a first reactor or reaction zone is passed into

25 a second reactor or reaction zone, wherein further monomer and catalyst are added.

To the extent that little if any live catalyst is passed from a first reactor or zone into a second reactor or zone, the product

30 emerging from a second reactor or zone is predominantly, if not completely, a combination of the individual polymers prepared separately in each reactor or zone, just as when the reactors are run in parallel. However, the ethylene polymers described herein are considered to include the resulting product should it happen that

35 monomer is polymerized onto the same polymer chain in both a first and second reactor or zone.

After the product streams from parallel reactors are combined, or after product emerges from the final reactor or zone in a series,

The ethylene polymer may be an ethylene homopolymer, or may be an interpolymer of ethylene and one or more  $C_3$ - $C_{20}$   $\alpha$ -olefin comonomers and/or one or more  $C_4$ - $C_{12}$  diolefins. The ethylene polymer can also be an interpolymer of ethylene with at least one of the above  $C_3$ - $C_{20}$  alpha olefins and/or diolefins in combination with other unsaturated monomers. Frequently, the ethylene polymer will be an interpolymer of ethylene with just one  $C_3$ - $C_{20}$   $\alpha$ -olefin, and are more preferably will be an interpolymer of ethylene with propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene or 1-octene, with an interpolymer of ethylene and 1-octene being especially preferred. Other preferred monomers for interpolymerization include styrene, halo or alkyl substituted styrenes, vinylbenzocyclobutene, 1,4 hexadiene, and naphthenics (e.g. cyclopentene, cyclohexene and cyclooctene).

Preferred ethylene polymers will comprise from 50 to 95 weight percent ethylene and from 5 to 50, and preferably from 10 to 25, weight percent of at least one comonomer. Comonomer content is measured using infrared spectroscopy according to ASTM D-2238, Method B.

The density of the ethylene polymer is measured in accordance with ASTM D-792, and is generally at least about  $0.85 \text{ g/cm}^3$ , is frequently at least about  $0.865 \text{ g/cm}^3$ , and is occasionally at least about  $0.89 \text{ g/cm}^3$ . The density of the ethylene polymer is generally  $0.96 \text{ g/cm}^3$  or less, is frequently  $0.93 \text{ g/cm}^3$  or less, and is occasionally  $0.90 \text{ g/cm}^3$  or less. The density measurement is often made of the polymer neat, i.e. a polymer without inorganic fillers and not containing in excess of 20 ppm aluminum from catalyst residue.

In certain instances, the ethylene polymers described herein are crystalline and/or semi-crystalline polymers. They are normally solid at room temperature, and are pelletizable at ambient conditions or at temperatures induced by cooled water. For example, a substantially linear ethylene/1-octene copolymer having a density of  $0.865 \text{ g/cm}^3$  has about 10% crystallinity at room temperature.

is the preferred ethylenically unsaturated organic compound containing at least one carbonyl group.

Ethylenically Unsaturated Functionalized Organic Compounds

5 Containing at Least One Epoxy Ring. Representative examples of ethylenically unsaturated organic compounds containing at least one epoxy ring include, for example, glycidyl esters of unsaturated carboxylic acids (e.g. glycidyl methacrylate); glycidyl ethers of unsaturated alcohols (e.g. allyl-glycidyl-ether) and of alkenylpheno  
10 ls (e.g. isopropenylphenyl-glycidylether); and vinyl and allyl esters of epoxycarboxylic acids (e.g. vinyl esters of epoxidized oleic acid). Other ethylenically unsaturated organic compounds containing at least one epoxy ring are described in Laughner, US-A-5,369,154, which is incorporated herein. Of these, glycidyl methacrylate is preferred.

15

Ethylenically Unsaturated Functionalized Organic Compounds

Containing at Least One Amine Functionality. Representative of the amines are amine compounds having at least one ethylenically unsaturated group, for instance, allyl amine, propenyl amine, butenyl  
20 amine, pentenyl amine, hexenyl amine; amine ethers including isopropenylphenyl ethyl amine ether and its homologues (branched, cyclic and unbranched), vinyl and allyl ethers of amine compounds, vinyl and allyl esters of amine substituted acids and the like. In each case, the amine and unsaturation are in any position in which  
25 they do not undesirably interfere with the graft reactions. Additionally, the amines are unsubstituted or optionally substituted with any groups such as alkyl groups (preferably of from about 1 to about 20 carbon atoms), aryl groups (preferably of from about 6 to about 30 carbon atoms), halogen, ether, thioether groups and the like  
30 which do not undesirably interfere with the grafting reactions.

Ethylenically Unsaturated Organic Compounds Containing at Least One Alcohol Functionality. Representative of the alcohols are any

35 compound, having a hydroxyl group and at least one ethylenically unsaturated group, for instance allyl and vinyl ethers of alcohol compounds like ethyl alcohol and its homologues (branched cyclic and

any solvent is removed, as is known in the art, to recover all the polymer together as one product.

5 The various reactors or zones which are run in series or parallel may differ with respect to features such as the type of catalyst used in each, the type of  $\alpha$ -olefin comonomer fed to each, or the temperature at which each is run. For example, a constrained geometry catalyst could be used in one reactor or zone and a Ziegler catalyst could be used in another. When reactors are run in parallel, 10 the combined stream or effluent from which the final product is recovered need not contain an equal portion of the output of each reactor.

15 Concerning Subcomponent (b), The Ethylenically Unsaturated Functionalized Organic Compound:

Subcomponent (b), the ethylenically unsaturated functionalized organic compound used in the preparation of the branched block ethylene polymers of this invention, will contain a carbon-carbon 20 double bond, and will form a branch off of a narrow polydispersity ethylene polymer by, for example, grafting thereto. These ethylenically unsaturated functionalized organic compounds are functionalized, containing functional groups, for example, such as a carbonyl group ( $-C=O$ ), (e.g. carboxylic acid or anhydride) or an epoxy 25 ring, an amine, or an alcohol, or the ethylenically unsaturated functionalized organic compound may be an oxazoline.

Ethylenically Unsaturated Functionalized Organic Compounds Containing at Least One Carbonyl Group. Representative of such 30 compounds which contain at least one carbonyl group are the unsaturated carboxylic acids, and their esters, anhydrides and salts (both metallic and nonmetallic) thereof. Preferably, the organic compound contains ethylenic unsaturation conjugated with a carbonyl group. Representative compounds include acrylic, methacrylic, maleic, 35 fumaric, itaconic, crotonic, methyl crotonic and cinnamic acid, and their ester, anhydride and salt derivatives, if any. Maleic anhydride



functionalized ethylenically unsaturated organic compound is present as a branch point to react with the reactive thermoplastic polymer of subcomponent (c) to form the branched block ethylene polymer of the invention.

5

The ethylenically unsaturated functionalized organic compound can be grafted to the ethylene polymer by any known technique within the skill in the art, such as those taught in USP 3,236,917 and USP 5,194,509. For example, in the '917 patent the polymer is introduced  
10 into a two-roll mixer and mixed at a temperature of 60°C. The ethylenically unsaturated organic compound is then added along with a free radical initiator, such as, for example, benzoyl peroxide, and the components are mixed at 30°C until the grafting is completed. In  
15 the '509 patent, the procedure is similar except that the reaction temperature is higher, e.g., 210 to 300°C, and a free radical initiator is not used or is used at a reduced concentration.

An alternative and preferred method of grafting is taught in USP 4,950,541, by using a twin-screw devolatilizing extruder as the mixing  
20 apparatus. The ethylene polymer and ethylenically unsaturated organic compound are mixed and reacted within the extruder at temperatures at which the reactants are molten and in the presence of a free radical initiator. Preferably, the ethylenically unsaturated organic compound is injected into a zone maintained under pressure within the extruder.

25

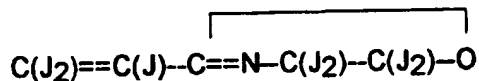
Concerning Subcomponent (c), The Reactive Thermoplastic Polymer:

Subcomponent(c), the reactive thermoplastic polymer utilized in the preparation of the branched block ethylene polymers of this  
30 invention, is suitably produced by the condensation of bifunctional monomers or other means within the skill in the art.

The reactive thermoplastic polymer is advantageously a semicrystalline or amorphous polymer containing functional groups that  
35 can react with the functionalized ethylene copolymer in a melt mixing process. Semicrystalline polymers preferably have  $T_m > 70^\circ\text{C}$ . Amorphous

unbranched) as well as vinyl and allyl esters of alcohol substituted, preferably carboxylic, acids as well as such compounds as propenyl alcohol, butenyl alcohol, pentenyl alcohol, hexenyl alcohol, heptenyl alcohol, octenyl alcohol. In each case, the alcohol and unsaturation are in any position in which they do not undesirably interfere with the graft reactions. Additionally, the alcohols are unsubstituted or optionally substituted with any groups such as alkyl groups (preferably of from about 1 to about 20 carbon atoms), aryl groups (preferably of from about 6 to about 30 carbon atoms), halogen, ether, thioether groups and the like which do not undesirably interfere with the grafting reactions.

Oxazoline Compounds for Use as the Ethylenically Unsaturated Functionalized Organic Compound. Representative oxazoline compounds for use herein include those of the general formula



where each J is independently hydrogen, halogen, a C<sub>1</sub>-C<sub>10</sub> alkyl radical or a C<sub>6</sub>-C<sub>14</sub> aryl radical.

The ethylenically unsaturated functionalized organic compound is used in an amount such that, after addition to the ethylene polymer to form the branched ethylene polymer, the portion of the branched ethylene polymer derived from the vinyl compound constitutes by weight, at least about 0.01 percent, preferably at least about 0.1 percent, and more preferably at least about 0.2 percent, and yet not more than about 10 percent, preferably not more than about 5 percent, and more preferably not more than about 2 percent of the ethylenically unsaturated organic compound.

Non-functionalized vinyl compounds (for example, an ethylenically unsaturated aromatic compound such as styrene) may be substituted for a portion of the ethylenically unsaturated functionalized organic compound, provided that enough

known as amine-functionalized polymers. One variety of amine-functionalized polymer is a polyamide, which may be produced by the condensation of bifunctional monomers, typically those containing acid and amine functionalities, where the monomers have either the same or different functional groups. For example, if hexamethylenediamine is reacted with adipic acid, an -[-AABB]- type polyamide is obtained wherein the diamine and diacid units alternate. However, when a monomer such as an amino acid or a cyclic lactam is self-polymerized, an -[-AB]- type polyamide results from a regular head-to-tail polymerization, similar to an addition mechanism. For example, when Nylon-6 is made, heat is applied to raise the temperature of the caprolactam to 240-280°C, and catalysts such as water and phosphoric acid are added to the system. Hydrolysis ensues, the ring opens and polymerization takes place while unreacted monomer is removed from the system and recycled. Polycondensation and growth of the polymer chain results from the removal of water from the system.

The polyamides suitable for use herein also include those wherein two or more different diamines, and/or different diacids and/or different amino acids are polymerized together to form a random or block co-polyamide. The carbon chain between the functional groups may be linear or branched aliphatic, alicyclic or aromatic hydrocarbons. The chains may also contain hetero atoms such as oxygen, sulfur or nitrogen. Also suitable for use herein are block or random copolymers, such as those resulting, for example, from melt mixing two or more different polyamides, from reaction of a diamine or diacid monomer that contains an amide linkage with another diamine or diacid, or from reaction of a diisocyanate with a dicarboxylic acid.

Polyamides are most often prepared by direct amidation in which the amine group of a diamine or an amino acid bonds to the carboxyl of a diacid with the accompanying elimination of water. Derivatives of the acid function, such as an ester, acyl halide or amide, may be used as an alternative source of the carboxyl functionality, in which case the by-product is an alcohol, a hydrogen halide or ammonia, respectively. Formation of polyamides can also occur by ring-opening polymerization of a caprolactam, such as when Nylon-6 is made from a caprolactam. Suitable polyamides are Nylon-11, Nylon-12, and in general nylon with a crystalline melting point less than 280°C, often

polymers preferably have  $T_g > 50^\circ\text{C}$ . Suitable functional groups include hydroxyl, phenolic, amine, epoxy, and isocyanate. Examples of suitable reactive thermoplastic polymers include polybutyleneterephthalate (PBT), polyethyleneterephthalate (PET),

5 Nylon-6, polysulfone, polyurethane, polycarbonate, polymethylmethacrylate functionalized with epoxy, styrene acrylonitrile functionalized with epoxy, or other functional groups, preferably those listed above.

10 Typically, the reactive thermoplastic polymer is used in an amount such that, after addition to the branched ethylene polymer to form a branched ethylene block polymer, the portion of the branched ethylene block polymer derived from the reactive thermoplastic polymer constitutes by weight, at least about 1  
15 percent, preferably at least about 2 percent, and more preferably at least about 5 percent, and yet not more than about 40 percent, preferably not more than about 30 percent, and more preferably not more than about 25 percent of the branched block ethylene polymer.

20

One suitable class of reactive thermoplastic polymers is the class known as engineering thermoplastics. The third edition of the Kirk-Othmer Encyclopedia of Science and Technology defines engineering plastics as thermoplastic resins, neat or unreinforced or filled,  
25 which maintain dimensional stability and most mechanical properties above  $100^\circ\text{C}$  and below  $0^\circ\text{C}$ . The terms "engineering plastics" and "engineering thermoplastics", can be used interchangeably.

Engineering Thermoplastics include acetal resins, polyamides (e.g. nylons), polyimides, polyetherimides, polyesters, liquid crystal  
30 polymers, and selected polyolefins, blends, or alloys of the foregoing resins, and some examples from other resin types (including e.g. polyethers) high temperature polyolefins such as polycyclopentanes, its copolymers, and polymethylpentane.)

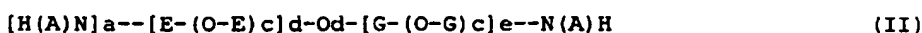
35 Concerning the Use of Amine-Functionalized Polymers as Subcomponent (c). One particularly suitable class of reactive thermoplastic polymers for use as subcomponent (c) is the class

923,255, filed October 27, 1986. In another suitable process, the corresponding hydroxyl- or primary amine-terminated polyether or polyester can be reacted in a transesterification reaction with a material such as a lower alkyl ester of p-aminobenzoic acid, particularly the methyl ester, to generate an aromatic polyamine compound. Secondary aromatic polyamines can be prepared in a Michael reaction of the corresponding primary aromatic amine compound and an ethylenically unsaturated compound such as acrylonitrile, as described above.

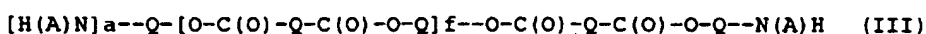
Blocked primary aliphatic polyamines suitable for use herein are advantageously prepared in the reductive amination of the corresponding hydroxyl-terminated compound with ammonia, followed by the complexation thereof with a Lewis acid such as benzoyl chloride, carbon dioxide, a metal carboxylate such as a tin, zinc, titanium or aluminum carboxylate, and the like. The Lewis acid is advantageously used in amounts of about 0.2 to about 5, and preferably about 0.9 to about 1.5, equivalents per equivalent of primary amine group.

Various amine-functionalized polymers suitable for use herein may be described by formula as:

20



25



where

- A is independently in each instance hydrogen or a  $C_1-C_6$  linear or branched alkyl or alkylene radical, optionally interruptable with one or more nitrogen or oxygen atoms, wherein each carbon atom is optionally substituted with a primary or secondary amine group;
- E is independently in each instance a  $C_1-C_{20}$ , preferably a  $C_1-C_{12}$ , and more preferably a  $C_1-C_8$  linear, branched or cyclic alkyl or alkylene radical, optionally interruptable with one or more nitrogen or oxygen atoms, wherein each carbon atom is optionally substituted with a halogen atom (such as a fluorine, chlorine, bromine or iodine atom), a  $C_1-C_6$  alkoxy group, a  $C_6-C_{10}$  aryloxy

less than 250°C, and occasionally less than 230°C, or amorphous nylon.

Polyamides as described above, and methods for preparing same, are discussed in greater detail in U.S. Pats. No. 2,071,253, 2,130,523 and 2,130,948.

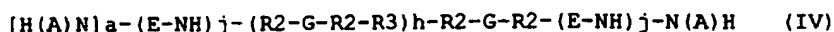
Other varieties of amine-functionalized polymers include amine-terminated butadiene/acrylonitrile rubber; or those polymers which have one or more primary aromatic, Lewis acid-blocked primary aliphatic and/or secondary aliphatic, or aromatic amine groups. Especially suitable amine-functionalized polymers are polyethers or polyesters having such amine groups.

Suitable polyols, especially polyether and polyester polyols, which have secondary amine groups are conveniently prepared by reacting the corresponding polyol with a primary amine, and reducing the resulting intermediate with hydrogen, as described in U.S. Patent No. 4,153,381. The secondary amine is advantageously an inertly substituted alkyl-, cycloalkyl- or benzyl-amine. Alternatively, secondary aliphatic polyamine compounds can be prepared in a Michael addition reaction of the corresponding primary aliphatic amine with an ethylenically unsaturated compound. Acrylonitrile is an especially suitable ethylenically unsaturated compound, although any compound which undergoes a Michael addition reaction with the primary amine can be used. The primary aliphatic amine itself can be prepared in the reductive amination of the corresponding polyol with ammonia, as taught, for example, in U.S. Patent Nos. 3,128,311, 3,152,998, 3,654,370, 3,347,926, 4,014,933.

Other suitable amine-functionalized polymers are aromatic polyamines, and include polyols, especially polyether and polyester polyols, which have been modified to contain aromatic amine groups. Such aromatic polyamines can be prepared, for example, by capping the corresponding polyether or polyester polyol with a diisocyanate to form a prepolymer, and then reacting the prepolymer with water to hydrolyze the free isocyanate groups to the corresponding primary amine. Alternatively, such compounds can be prepared by reacting the corresponding polyether or polyester polyol with p-nitro chlorobenzene, followed by the reduction of the nitro group to the amine, as taught in the application of Steuber et al, Serial No.

30, inclusive;  
 d and e are both 0 or 1, although d and e cannot both be 0; and  
 f is 0 to 70, preferably 5 to 50, and more preferably 5 to  
 30, inclusive; or

5



where

- 10 R<sub>2</sub> is independently in each instance an  
 -E-CH(OH)-E- radical;  
 R<sub>3</sub> is independently in each instance an  
 -HN-(E-NH)<sub>j</sub>- radical;  
 A, E, G, a are as set forth above;  
 15 h is 0 to 25, preferably 0 to 10, and more preferably  
 1 to 3, inclusive; and  
 j is 1 to 6, and preferably 1 to 4, inclusive.

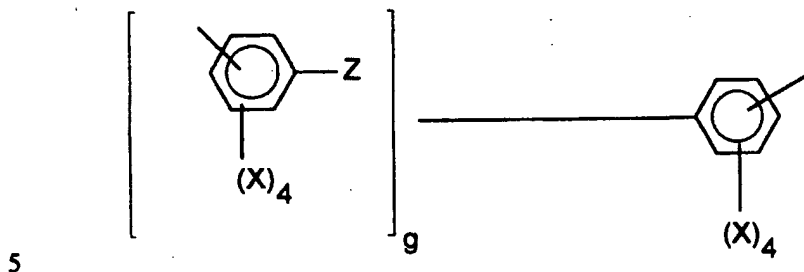
- 20 Numerical variables in the above formulae may take on individual  
 values within the ranges specified or subranges other than those  
 specifically set forth.

- 25 The amine-functionalized polymer will have an average number of  
 amine groups per molecule which is generally about 0.75 or more, is  
 preferably about 0.8 or more, is more preferably about 0.9 or more,  
 and is most preferably about 1.0 or more. The amine-functionalized  
 polymer will have an average number of amine groups per molecule which  
 is generally about 3.5 or less, is preferably about 3.0 or less, is  
 more preferably about 2.5 or less, and is most preferably about 2.1 or  
 30 less.

- The amine-functionalized polymer will typically have an  
 equivalent weight (defined as weight average molecular weight divided  
 by average number of amine groups) of about 400 to about 50,000,  
 35 preferably about 600 to about 30,000, and more preferably about 800 to  
 about 20,000.

The amine-functionalized polymer will be present in an  
 amount sufficient to form the final block of the branched block

group, a phenyl group, or a primary or secondary amine group;  
 G is independently in each instance described by the following structure:



wherein:

- 10 (I) Z is (A) a divalent radical, of which all or different portions can be (i) linear, branched, cyclic or bicyclic, (ii) aliphatic or aromatic, and/or (iii) saturated or unsaturated, said divalent radical being composed of 1-35 carbon atoms together with up to five oxygen, nitrogen, sulfur, phosphorous and/or halogen (such as fluorine, chlorine and/or bromine) atoms, wherein each carbon atom is optionally substituted with a primary or secondary amine group; or (B) S, S<sub>2</sub>, SO, SO<sub>2</sub>, O or CO; or (C) a single bond, and
- 15
- 20 (II) each X is independently hydrogen, a halogen atom (such as fluorine, chlorine and/or bromine), a C<sub>1</sub>-C<sub>12</sub> linear or cyclic alkyl, alkoxy, aryl or aryloxy radical, such as methyl, ethyl, isopropyl, cyclopentyl, cyclohexyl, methoxy, ethoxy, benzyl, tolyl, xylyl, phenoxy and/or xylynoxy; or primary or secondary amine group; and
- 25
- (III) g is 0 or 1;

- Q is independently in each instance E or G;
- 30 a is 0 or 1;
- b is 0 to 10, preferably 0-4, and more preferably 1 to 3, inclusive, although a and b cannot both be 0;
- c is 1 to 70, preferably 5 to 50, and more preferably 5 to



hydroxycarboxylic acids, or by direct esterification, which involves the step-growth reaction of a diol with a dicarboxylic acid with the resulting elimination of water, giving a polyester with an  $[-AABB-]$  repeating unit. The reaction may be run in  
5 bulk or in solution using an inert high boiling solvent such as xylene or chlorobenzene with azeotropic removal of water.

Alternatively, but in like manner, ester-forming derivatives of a dicarboxylic acid can be heated with a diol to obtain polyesters in  
10 an ester interchange reaction. Suitable acid derivatives for such purpose are alkyl esters, halides, salts or anhydrides of the acid. Preparation of polyarylates, from a bisphenol and an aromatic diacid, can be conducted in an interfacial system which is essentially the same as that used for the preparation of polycarbonate.

15 Polyesters can also be produced by a ring-opening reaction of cyclic esters or  $C_4$ - $C_7$  lactones, for which organic tertiary amine bases, phosphines and alkali and alkaline earth metals, hydrides and alkoxides can be used as initiators.

Suitable reactants for making the polyester used in this  
20 invention, in addition to hydroxycarboxylic acids, are diols and dicarboxylic acids either or both of which can be aliphatic or aromatic. A polyester which is a poly(alkylene alkanedicarboxylate), a poly(alkylene arylenedicarboxylate), a poly(arylene alkanedicarboxylate), or a poly(arylene arylenedicarboxylate) is  
25 therefore appropriate for use herein. Alkyl portions of the polymer chain can be substituted with, for example, halogens,  $C_1$ - $C_8$  alkoxy groups or  $C_1$ - $C_8$  alkyl side chains and can contain divalent heteroatomic groups (such as  $-O-$ ,  $-Si-$ ,  $-S-$  or  $-SO_2-$ ) in the paraffinic segment of the chain. The chain can also contain unsaturation and  $C_6$ - $C_{10}$  non-  
30 aromatic rings. Aromatic rings can contain substituents such as halogens,  $C_1$ - $C_8$  alkoxy or  $C_1$ - $C_8$  alkyl groups, and can be joined to the polymer backbone in any ring position and directly to the alcohol or acid functionality or to intervening atoms.

ethylene polymers of the invention, without being present in such a high quantity that the desired benefit of the branched block ethylene polymer as a compositional modifier is sacrificed. Typically, the amine-functionalized polymer is used in an amount such that, after addition to the branched ethylene polymer to form a branched ethylene block polymer, the portion of the branched ethylene block polymer derived from the amine-functionalized polymer constitutes by weight, at least about 1 percent, preferably at least about 2 percent, and more preferably at least about 5 percent, and yet not more than about 40 percent, preferably not more than about 30 percent, and more preferably not more than about 25 percent of the branched block ethylene polymer.

For example, it would not ordinarily be expected that a crystalline, polar, amine-functionalized polymer such as polyamide would improve the performance of a non-polar ethylene polymer as a modifier in a blend with a thermoplastic molding polymer. However, it has been found that when an amine-functionalized polymer, such as polyamide, is used in the amounts stated above, it not only forms the final block of the branched block ethylene polymer, but remains morphologically dispersed within domains formed by an ethylene/vinyl compound copolymer. However, if an amine-functionalized polymer such as polyamide is used in amounts exceeding the above-recommended amounts, it tends to form crystalline domains of its own in which an ethylene/vinyl compound copolymer is dispersed, and the brittleness of those polyamide domains offsets the gain in impact strength which a block terpolymer would otherwise impart to the blended composition. Correspondingly, if an amine-functionalized polymer which has too high an average amine functionality is used, crosslinking is likely to occur.

Concerning the Use of a Polyester as the Reactive  
Thermoplastic Polymer of Component (c):

A further class of reactive thermoplastic polymers useful as subcomponent (c) of the branched block ethylene polymers are polyesters. Polyesters may be made by the self-esterification of

Methods and materials useful for the production of polyesters, as described above, are discussed in greater detail in Whinfield, USP 2,465,319, Pengilly, USP 3,047,539, Schwarz, USP 3,374,402, Russell, USP 3,756,986 and East, USP 4,393,191.

5

In a preferred embodiment, a polyester is used in an amount such that, after addition to an ethylene/vinyl compound copolymer to form a branched block ethylene polymer, the portion of the branched block ethylene polymer derived from the polyester constitutes by weight, at least about 1 percent, preferably at least about 2 percent, and more preferably at least about 5 percent, and yet not more than about 30 percent, preferably not more than about 20 percent, and more preferably not more than about 10 percent of the branched block ethylene polymer. In other embodiments, when for example a catalyst is used to accelerate formation of a branched block ethylene polymer, the amount of polyester used may constitute more than about 60, possibly more than about 70, or perhaps more than about 80 weight percent of the branched block ethylene polymer, but values outside these ranges are permitted as well. In a further preferred embodiment, the polyester is used in an amount such that the weight ratio between the amount of polyester contained in the branched block ethylene polymer and the amount of blending or molding polymer contained in the composition is greater than about 0.01/1, is often greater than about 0.015/1, and occasionally greater than about 0.02/1, and yet is less than about 0.30/1, is often less than about 0.15/1, and is occasionally less than 0.10/1.

In a further preferred embodiment, the polyester used for preparation of a branched block ethylene polymer has an intrinsic viscosity (IV) of less than about 0.85, advantageously about 0.5 to about 0.8, and preferably about 0.55 to about 0.75. A polyester having a relatively low IV is in general composed of shorter polymer chains than a polyester of relatively high IV. A particular mass of low IV polyester will therefore contain more

Typical aliphatic diols used in ester formation are the C<sub>2</sub>-C<sub>10</sub> primary and secondary glycols, such as ethylene-, propylene-, and butylene glycol. Alkanedicarboxylic acids frequently used are oxalic acid, adipic acid and sebacic acid. Diols which contain rings can be, for example, a 1,4-cyclohexylenyl glycol or a 1,4-cyclohexane-dimethylene glycol, resorcinol, hydroquinone, 4,4'-thiodiphenol, bis-(4-hydroxyphenyl)sulfone, a dihydroxynaphthalene, a xylylene diol, or can be one of the many bisphenols such as 2,2-bis-(4-hydroxyphenyl)propane. Aromatic diacids include, for example, terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, diphenyletherdicarboxylic acid, diphenyldicarboxylic acid, diphenylsulfonedicarboxylic acid, diphenoxyethanedicarboxylic acid.

In addition to polyesters formed from one diol and one diacid only, the term "polyester" as used herein includes random, patterned or block copolyesters, for example those formed from two or more different diols and/or two or more different diacids, and/or from other divalent heteroatomic groups. Mixtures of such copolyesters, mixtures of polyesters derived from one diol and diacid only, and mixtures of members from both of such groups, are also all suitable for use in this invention, and are all included in the term "polyester". For example, use of cyclohexanedimethanol together with ethylene glycol in esterification with terephthalic acid forms a clear, amorphous copolyester of particular interest. Also contemplated are liquid crystalline polyesters derived from mixtures of 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid; or mixtures of terephthalic acid, 4-hydroxybenzoic acid and ethylene glycol; or mixtures of terephthalic acid, 4-hydroxybenzoic acid and 4,4'-dihydroxybiphenyl.

Aromatic polyesters, those prepared from an aromatic diacid, such as the poly(alkylene arylenedicarboxylates) polyethylene terephthalate and polybutylene terephthalate, or mixtures thereof, are particularly useful in this invention. A polyester suitable for use herein may have an intrinsic viscosity of about 0.4 to 1.2, although values outside this range are permitted as well.

When using an extruder for preparation of a branched block ethylene polymer, the separate components from which it is prepared are typically fed in sequence through separate ports during a single pass through one extruder for more convenient material handling. If the ethylene polymer, ethylenically unsaturated organic compound, and reactive thermoplastic polymer are reacted simultaneously, it is probable that the ethylenically unsaturated organic compound will form an insignificant amount of branching on the ethylene polymer, or none at all, because the presence of the reactive thermoplastic polymer can physically hinder the necessary access of unsaturated organic compound for branch formation.

The Use of Catalysts in the Preparation of the Block Ethylene Polymers of the Invention:

Reaction between the branched ethylene polymer and the reactive thermoplastic polymer to complete preparation of the branched block ethylene polymers of the invention is optionally enhanced by the presence of a catalyst. Such catalysts may include an alkali metal or alkaline earth metal salt having a pKa of 7 or more and a nitrogen-containing organic base. Those catalysts which melt at or below the temperature at which the branched ethylene polymer and reactive thermoplastic polymer are being reacted, and which have low volatility at that temperature, will be most effective.

Salts having a pKa of 7 or more, useful as a catalyst herein, are those formed from cations of which the following are representative examples:

lithium, sodium, potassium, magnesium, calcium or barium;  
and from anions of which the following are representative examples:  
azide, acetate, benzoate, borate, bromate, bromide, carbonate, carboxylate, chlorate, chloride, chlorite, chromate, cyanate, cyanide, dithionate, fluoride, formate, hydrogen carbonate, hydrogen phosphate, hydrogen sulfate, hydrogen sulfide, hydrogen sulfite, hydroxide, hypophosphate, hypophosphite, iodate, iodide, iodite, molybdate, nitrate, nitrite, oxalate, oxide,

chain end groups than will the same mass of high IV polyester. Since formation of a branched block ethylene polymer is dependent on the reaction of polyester end groups, especially -OH end groups, with the branch point formed from a vinyl compound on an  
5 ethylene polymer, it is advantageous to use a polyester for this purpose which contains a relatively large number of end groups.

Process for Preparing the Branched Block Ethylene Polymers of the Invention:

10

The branched block ethylene polymers of this invention are prepared by first forming a branch containing the ethylenically unsaturated functionalized organic compound off of the ethylene polymer. This may be accomplished by the techniques set forth above,  
15 e.g., using the methods of graft polymerization taught in USP 3,236,917, USP 5,194,509, and/or USP 4,950,541.

After the ethylenically unsaturated functionalized organic compound, such as maleic anhydride, has been formed into a branch off  
20 of the ethylene polymer, preparation of the branched block ethylene polymer of this invention can be completed by subjecting the branched ethylene polymer and the reactive thermoplastic polymer to reactive extrusion. Reactive end groups on the reactive thermoplastic polymer react in the melt state with the functionality of the functionalized  
25 organic compound branch to form a chemical bond and add the final polymer block to the branched block ethylene polymers of this invention. This reaction between reactive thermoplastic polymer and the branch formed from the ethylenically unsaturated functionalized organic compound may be enhanced by a catalyst, if desired. Although  
30 this reaction optionally occurs in a Banbury mixer or other apparatus in which elevated temperature and high shear mixing can be applied to the reactants, a representative profile for conducting this reaction in a 30 mm twin screw extruder is: zone temperatures of 150, 200, 250, 250 and 250°C; 250 rpm; 70-85 percent torque; and 30 second  
35 residence time.

based on the combined weight of the branched ethylene polymer and the reactive thermoplastic polymer.

5     Concerning the Blending of the Branched Block Ethylene Polymers with an Additional Blending or Molding Polymer:

10     The branched block ethylene polymers of the invention may advantageously be dry blended or melt blended with one or more additional blending or molding polymers. In one instance the branched block ethylene polymer will be dry blended or melt blended with a blending or molding, and then molded or extruded into a shaped article.

15     It is noted from the exemplary polymers shown in the Figures that branched block ethylene polymers of the invention are effective rheology modifiers, effective melt strength enhancers, blow molding or thermoforming strength enhancers, effective oil extended polymers, and/or impact modifiers.

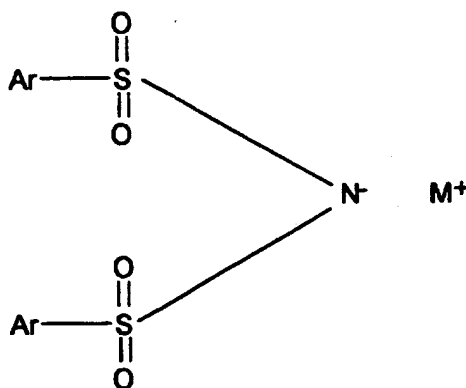
20     It is further noted that the formation of a random, physical blend from a ethylene polymer which has been graft-modified by an ethylenically unsaturated functionalized monomer, a reactive thermoplastic polymer and a thermoplastic blending or molding polymer, is separate and distinct from the blend of a branched block ethylene polymer and such blending or molding polymer. The distinction can be appreciated by examining systems comprising an ethylene polymer, ethylenically unsaturated functionalized monomer, amine-functionalized polymer, and blending or molding thermoplastic polymer.

30     In the case of a random, physical blend, an ethylene polymer which has been graft modified with the ethylenically unsaturated functionalized polymer may be used as an essentially elastomeric modifier for one or more thermoplastic polymers, one of which might be an amine-functionalized polymer. In the case where two or more thermoplastic polymers are present in the composition, the ethylene polymer which has been graft modified with the ethylenically unsaturated functionalized polymer will

perchlorate, permanganate, phosphate, phosphite, pyrophosphate, selenate, silicate, sulfate, sulfimide, sulfite, sulfonate, thiocarbonate, thiocyanate, thiosulfate, and the like, in both substituted and unsubstituted form, and derivatives thereof.

5

A preferred salt for use as a catalyst herein may be derived from an aromatic sulfimide, as shown in the following structure where  $M^+$  is an alkali metal ion, for example potassium ion.



10

Representative nitrogen-containing organic bases useful as a catalyst herein may include acridine, analine, aziridine, benzidine, benzimidazole, isoquinoline, morpholine, picoline, piperazine, piperidine, purine, pyrazine, pyridine, pyrimidine, pyrrolidine, quinazoline, quinoline, toluidine, valine, and the like. In general, many aliphatic and aromatic amines, in both substituted and unsubstituted form, and derivatives thereof, may serve as a catalyst herein, the most common being tertiary amines such as triethylamine and pyridine.

25

The amount of the catalyst used in preparation of the branched block ethylene polymers of the invention is, by weight, at least about 100 ppm, and preferably at least about 1,000 ppm, and yet not more than about 3,000 ppm, and preferably not more than about 2,000 ppm,



copolymer, polyisobutylene, ethylene-propylene-diene monomer (EPDM), polystyrene, acrylonitrile-butadiene-styrene (ABS) copolymer, ethylene/acrylic acid (EAA), ethylene/vinyl acetate (EVA), ethylene/vinyl alcohol (EVOH), polymers of ethylene and carbon  
5 monoxide (ECO, including those described in USP 4,916,208), or ethylene, propylene and carbon monoxide (EPCO) polymers, or ethylene, carbon monoxide and acrylic acid (ECOAA) polymers, and the like. Representative of the non-olefin blending or molding polymers are the polyesters, polyvinyl chloride (PVC), epoxies, polyurethanes,  
10 polycarbonates, polyamides, and the like.

The exemplary blending or molding polymers are characterized by a compatibility with the branched block ethylene polymer such that the melt blend does not separate into separate polymer phases. If more  
15 than one of these blending or molding polymers is blended with one or more branched block ethylene polymers, then all usually exhibit sufficient compatibility with each other, one-to-one or at least in combination with one or more other polymers, such that the polymeric components do not separate into separate polymer phases which could  
20 lead to extrusion processing difficulties, such as extrudate surging, film band-effects, etc.

The amount of branched block ethylene polymer that is blended with one or more other blending or molding thermoplastic polymers can  
25 be varied and is dependent upon many factors, including the nature of the blending or molding thermoplastic polymer or polymers, the intended end use of the blend, the presence or absence and if present, the nature, of additives, and the like.

Typically, the blend will comprise at least 1 part,  
30 advantageously at least about 2 parts, and preferably at least about 5 parts, and yet not more than about about 50 parts, advantageously not more than about 40 parts, and preferably not more than about 30 parts of the branched block ethylene polymer. Likewise, the blend will  
35 typically comprise at least about 50 parts, advantageously at least about 60 parts, and preferably at least about 70 parts, and yet not

typically serve as such elastomeric modifier for each thermoplastic polymer to an essentially equal extent. In contrast, when it is desired to use a branched block ethylene polymer as a modifier in a blend with a thermoplastic blending or molding polymer, if a branched block ethylene polymer is not successfully formed, the result is no different from a random, physical blend containing some amine-functionalized polymer as one of the molding polymers in which the ethylene polymer which has been graft-modified with the ethylenically unsaturated functionalized polymer serves as modifier for the entire content of molding polymer.

The reactive thermoplastic polymer is present first and foremost to alter the viscoelastic properties of the ethylene polymer which has been graft-modified with the ethylenically unsaturated functionalized monomer, and convert what was an essentially elastomeric modifier into a hard segment/soft segment modifier. The reactive thermoplastic polymer constitutes the hard segment, and the ethylene polymer constitutes the soft segment. This hard segment/soft segment modifier, the branched block ethylene polymer, then serves as a modifier for one or more blending or molding polymers. The reactive thermoplastic polymer in the branched block ethylene polymer, as an integral portion of the hard segment/soft segment modifier, performs a function which is distinct from that of being just another molding polymer in a random, physical blend.

Suitable blending or molding polymers include any polymer with which the branched block ethylene polymer is compatible, and include both olefin and non-olefin polymers, grafted and ungrafted. The branched block ethylene polymer can also be blended with a substantially linear ethylene polymer, a conventional heterogeneously branched or homogeneously branched linear ethylene polymer, a non-olefin polymer, any of which can be grafted or ungrafted, or any combination of these polymers.

Exemplary blending or molding polymers include high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), ultra low density polyethylene (ULDPE), polypropylene, ethylene-propylene copolymer, ethylene-styrene

1.5 MPa (5-15 atm), and the gas-phase and liquid-monomer processes, in which extra care must be given to the removal of amorphous polymer. Ethylene may be added to the reaction to form a polypropylene with ethylene blocks.

5

Various higher olefins can be homopolymerized to form polyolefin resins using Ziegler-Natta catalysts, representative examples thereof being 1-butene, 1-methyl-pentene and 4-methyl-1-pentene. The polyolefin resins useful herein also include various ethylene  
10 copolymers such as ethylene/acrylic acid copolymer, ethylene/vinyl acetate copolymer, ethylene/vinyl alcohol copolymer, ethylene/carbon monoxide copolymer (including those described in USP 4,916,208 and 4,929,673, ethylene/propylene/carbon monoxide copolymer, ethylene/carbon monoxide/acrylic acid copolymer, poly(vinyl chloride),  
15 and the like and mixtures thereof. For example, in the suspension process for preparing poly(vinyl chloride), vinyl chloride monomer can be copolymerized with other vinyl monomers, such as vinyl acetate, acrylonitrile, butadiene, butyl acrylate, maleic anhydride, an olefin or styrene, to produce a random, block or graft copolymer.

20

One particular advantage of using a polyamide resin, as the molding polymer is that it can be blended with a block terpolymer in a molding machine, and the addition of an extra heat history to the composition by first extruding pellets of a block terpolymer/molding  
25 polymer composition is thus avoided.

Use of Polyamides as the Blending or Molding Polymer. Polyamides useful as the thermoplastic polymer are described above as a variety of amine-functionalized polymer which may be used in preparation of a  
30 block terpolymer. When a polyamide is used as the molding polymer, it is possible, and sometimes preferred, to use a different polyamide from that which was used to prepare the block terpolymer. For example, the polyamide used to prepare the block terpolymer may be a Nylon 6, whereas the polyamide used as the molding polymer may be a  
35 Nylon 6,6; 6,10; or 12, and/or the blending or molding polymer may have an average number of amine groups greater than about 2.0, or in the range of about 2.05 to about 3.5. One particular advantage of using a polyamide resin, as the molding polymer is that it can be blended with a block terpolymer in a molding machine, and the addition

more than about 99 parts, advantageously not more than about 98 parts, and preferably not more than about 95 parts, of the blending or molding thermoplastic polymer or polymers. Note that the number of parts by weight of the branched block ethylene polymer and the  
5 blending or molding polymer or polymers may, but need not necessarily, total 100 parts by weight.

However, if the blending or molding polymer is identical in composition of the reactive thermoplastic polymer which forms a branch  
10 of the branched block ethylene polymer, the total amount of the reactive thermoplastic polymer and blending or molding thermoplastic polymer will exceed 30 parts, preferably 20 parts, more preferably 15 parts, and most preferably 10 parts, per 100 weight parts of the blended composition.

15

Preferred blending or molding polymers for use in conjunction with a branched block ethylene polymer which has as the reactive thermoplastic polymer a functionalized-amine polymer include (i) polyolefin resins, (ii) a polyamide, (iii) a polycarbonate, (iv) a  
20 hydrogenated polystyrene; and (v) a mixture thereof. Preferred blending or molding polymers for use in conjunction with a branched block ethylene polymer which has as the reactive thermoplastic polymer a polyester include (i) a polycarbonate, (ii) a polyester, (iii) a poly(phenylene ether), (iv) a polysulfone, (v) a polyimide or  
25 polyether imide, and (vi) a mixture thereof.

Use of Polyolefin Resins as the Blending or Molding Polymer.

Polyolefin resins useful as the thermoplastic polymer are any of the ethylene polymers described above with respect to preparation of  
30 branched block ethylene polymer, and polypropylene. The preparation of polypropylene also involves the use of Ziegler catalysts, which allows the stereo regular polymerization of propylene to form isotactic polypropylene. The catalyst used is typically a titanium trichloride in combination with aluminum diethylmonochloride, as  
35 further described in Cecchin, USP 4,177,160. The various types of polymerization processes used for the production of polypropylene include the slurry process, which is run at about 50 - 90°C and 0.5 -

phosgene, the products of this initial phase of the process are monomers or oligomers which are either mono- or dichloroformates, or contain a phenolate ion at each terminus.

5        These intermediate mono- and oligocarbonates dissolve in the organic solvent as they form, and they can then be condensed to a higher molecular weight polycarbonate by contact with a coupling catalyst of which the following are representative: a tertiary amine such as triethyl amine and dimethyl amino pyridine.

10        Upon completion of polymerization, the organic and aqueous phases are separated to allow purification of the organic phase and recovery of the polycarbonate product therefrom. The organic phase is washed as needed in a centrifuge with dilute base, water and/or dilute acid  
15        until free of unreacted monomer, residual process chemicals and/or other electrolytes. Recovery of the polycarbonate product can be effected by spray drying, steam devolatilization, direct devolatilization in a vented extruder, or precipitation by use of an anti-solvent such as toluene, cyclohexane, heptane, methanol, hexanol,  
20        or methyl ethyl ketone.

      In the melt process for preparation of polycarbonate, aromatic diesters of carbonic acid are condensed with an aromatic dihydroxy compound in a transesterification reaction in the presence of a basic  
25        catalyst. The reaction is typically run at about 250°C to 300°C under vacuum at a progressively reduced pressure of about 1 to 100 mm Hg.

      Polycarbonate can also be prepared in a homogeneous solution through a process in which a carbonate precursor, such as phosgene, is  
30        contacted with a solution containing an aromatic dihydroxy compound, a chlorinated hydrocarbon solvent and a substance, such as pyridine, for dimethyl aniline or  $\text{Ca}(\text{OH})_2$ , which acts as both acid acceptor and condensation catalyst.

35        Examples of some dihydroxy compounds suitable for the preparation of polycarbonate include variously bridged, substituted or unsubstituted aromatic dihydroxy compounds (or mixtures thereof)

of an extra heat history to the composition by first extruding pellets of a block terpolymer/molding polymer composition is thus avoided.

Use of Polycarbonates as the Blending or Molding Polymer.

5 Polycarbonates useful as the blending or molding polymer can be prepared from a dihydroxy compound such as a bisphenol, and a carbonate precursor such as a disubstituted carbonic acid derivative, a haloformate (such as a bishaloformate of a glycol or dihydroxy benzene), or a carbonate ester such as diphenyl carbonate or a  
10 substituted derivative thereof. These components are often reacted by means of the phase boundary process in which the dihydroxy compound is dissolved and deprotonated in an aqueous alkaline solution to form bisphenolate and the carbonate precursor is dissolved in an organic solvent.

15

These components are often reacted by means of a mixture prepared initially from the aromatic dihydroxy compound, water and a non-reactive organic solvent immiscible with water selected from among those in which the carbonate precursor and polycarbonate product are  
20 soluble. Representative solvents include chlorinated hydrocarbons such as methylene chloride, 1,2-dichloroethane, tetrachloroethane, chlorobenzene, and chloroform. Caustic soda or other base is then added to the reaction mixture to adjust the pH of the mixture to a level at which the dihydroxy compound is activated to dianionic form.

25

A carbonate precursor is contacted with an agitated mixture of the aqueous alkaline solution of the dihydroxy compound, and, for such purpose, the carbonate precursor can be bubbled into the reaction mixture in the form of a gas, or can be dissolved and introduced in  
30 solution form. Carbonate precursor is typically used in an amount of about 1.0 to 1.8, preferably about 1.2 to 1.5, moles per mole of dihydroxy compound. The mixture is agitated in a manner which is sufficient to disperse or suspend droplets of the solvent containing the carbonate precursor in the aqueous alkaline solution. Reaction  
35 between the organic and aqueous phases created by such agitation yields the bis(carbonate precursor) ester of the dihydroxy compound. For example, if the carbonate precursor is a carbonyl halide such as

hydroxyphenyl)propane ("Bisphenol-A" or "Bis-A"); 2,2-bis(3,5-dihalo-4-hydroxyphenyl)propane ("Tetrahalo Bisphenol-A") where the halogen can be fluorine, chlorine, bromine or iodine, for example 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane ("Tetrabromo Bisphenol-A" or "TBBA");  
5 2,2-bis(3,5-dialkyl-4-hydroxyphenyl)propane ("Tetraalkyl Bisphenol-A") where the alkyl can be methyl or ethyl, for example 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane ("Tetramethyl Bisphenol-A"); 1,1-bis(4-hydroxyphenyl)-1-phenyl ethane ("Bisphenol-AP" or "Bis-AP"); Bishydroxy phenyl fluorene; and 1,1-bis(4-hydroxyphenyl)cyclohexane.  
10

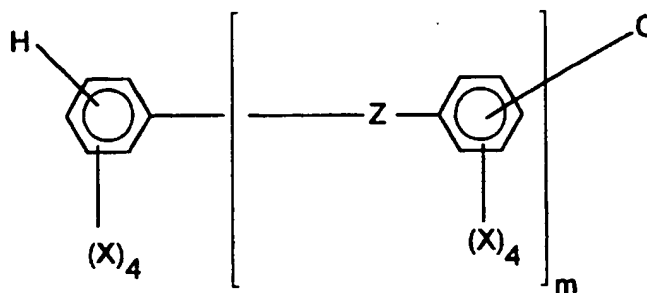
Using a process such as is generally described above, a polycarbonate product can be obtained having a weight average molecular weight, as determined by light scattering or gel permeation chromatography, of 8,000 to 200,000 and preferably 15,000 to 40,000,  
15 and/or a melt flow value of about 3 to 150, preferably about 10 to 80 (as determined by ASTM Designation D 1238-89, Condition 300/1.2), although values outside these ranges are permitted as well. Molecular weight can be controlled by addition to the reaction mixture of a chain terminator which may be selected from monofunctional substances  
20 such as phenols, carbonic acid chlorides, or phenylchlorocarbonates.

A branched rather than linear polycarbonate molecule can be obtained by adding to the reaction mixture a tri- or polyfunctional monomer such as trisphenoxy ethane.  
25

The preferred process of this invention is that in which an aromatic polycarbonate is prepared. An aromatic polycarbonate is defined herein with reference to the oxygen atoms, of the one or more dihydroxy compounds present in the polycarbonate chain, which are  
30 bonded to a carbonyl carbon of the carbonate precursor. In an aromatic polycarbonate, all such oxygen atoms are bridged by a dihydroxy compound residue some portion of which is an aromatic ring.

Also included within the term "polycarbonate", as used herein,  
35 are various copolycarbonates, certain of which can be prepared by incorporating one or more different dihydroxy compounds into the reaction mixture. When a dicarboxylic acid such terephthalic acid or

represented by the formula:



wherein:

- I) Z is (A) a divalent radical, of which all or different portions can be (i) linear, branched, cyclic or bicyclic, (ii) aliphatic or aromatic, and/or (iii) saturated or unsaturated, said divalent radical being composed of 1-35 carbon atoms together with up to five oxygen, nitrogen, sulfur, phosphorous and/or halogen (such as fluorine, chlorine and/or bromine) atoms; or (B) S, S<sub>2</sub>, SO, SO<sub>2</sub>, O or CO; or (C) a single bond;

- II) each X is independently hydrogen, a halogen (such as fluorine, chlorine and/or bromine), a C<sub>1</sub>-C<sub>12</sub>, preferably C<sub>1</sub>-C<sub>8</sub>, linear or cyclic alkyl, aryl, alkaryl, aralkyl, alkoxy or aryloxy radical, such as methyl, ethyl, isopropyl, cyclopentyl, cyclohexyl, methoxy, ethoxy, benzyl, tolyl, xylyl, phenoxy and/or xylynoxy; or a nitro or nitrile radical; and

(III) m is 0 or 1.

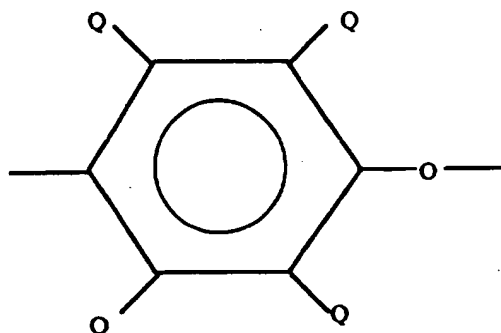
For example, the bridging radical represented by Z in the above formula can be a C<sub>2</sub>-C<sub>30</sub> alkyl, cycloalkyl, alkylidene or cycloalkylidene radical, or two or more thereof connected by an aromatic or ether linkage, or can be a carbon atom to which is bonded one or more groups such as CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, n-C<sub>3</sub>H<sub>7</sub>, i-C<sub>3</sub>H<sub>7</sub>, cyclohexyl, bicyclo[2.2.1]heptyl, benzyl, CF<sub>2</sub>, CF<sub>3</sub>, CCl<sub>3</sub>, CF<sub>2</sub>Cl, CN, (CH<sub>2</sub>)<sub>2</sub>COOCH<sub>3</sub>, or PO(OCH<sub>3</sub>)<sub>2</sub>.

Representative examples of dihydroxy compounds of particular interest are the bis(hydroxyphenyl)alkanes, the bis(hydroxyphenyl)cycloalkanes, the dihydroxydiphenyls and the bis(hydroxyphenyl)sulfones, and in particular are 2,2-bis(4-



Use of Poly(phenylene ether) as the Thermoplastic Polymer.

Suitable thermoplastic polymers include poly(phenylene ether) [also known as a poly(phenylene oxide)], which is a polymer comprising a plurality of structural units described generally by the formula:



In each of said units independently, each  $Q_1$  is independently hydrogen, halogen, primary or secondary  $C_1-C_8$  lower alkyl, phenyl, haloalkyl, aminoalkyl, hydrocarbonoxy, or halohydrocarbonoxy wherein at least two carbon atoms separate the halogen and oxygen atoms; and each  $Q_2$  is independently hydrogen, halogen, primary or secondary  $C_1-C_8$  lower alkyl, phenyl, haloalkyl, hydrocarbonoxy or halohydrocarbonoxy as defined for  $Q_1$ . Examples of suitable primary lower alkyl groups are methyl, ethyl, n-propyl, n-butyl, isobutyl, n-amyl, isoamyl, 2-methylbutyl, n-hexyl, 2,3-dimethylbutyl, 2-, 3- or 4-methylpentyl and the corresponding heptyl groups. Examples of secondary lower alkyl groups are isopropyl, sec-butyl and 3-pentyl. It is preferred that any alkyl radicals are straight chain rather than branched. Most often, each  $Q_1$  is alkyl or phenyl, especially  $C_1-C_4$  alkyl, and each  $Q_2$  is hydrogen.

Both homopolymer and copolymer poly(phenylene ether)s are included, as well as mixtures or blends thereof. Suitable

isophthalic acid (or an ester-forming derivative thereof) or a hydroxycarboxylic acid is used in the reaction mixture, or to form an oligomeric prepolymer, instead of one of the "different" dihydroxy compounds mentioned above, a poly(ester/carbonate) is obtained, which  
5 is discussed in greater detail in Swart, USP No. 4,105,533. In a preferred embodiment, the compositions of this invention exclude a poly(ester/carbonate).

Copolycarbonates can also be prepared, for example, by reaction  
10 of one or more dihydroxy compounds with a carbonate precursor in the presence of a chlorine- or amino-terminated polysiloxane, with a hydroxy-terminated poly(phenylene oxide) or poly(methyl methacrylate), or with phosphonyl dichloride or an aromatic ester of a phosphonic acid. Siloxane/carbonate block terpolymers are discussed in greater  
15 detail in Paul, USP 4,596,970.

The methods generally described above for preparing carbonate polymers suitable for use in the practice of this invention are well known; for example, several methods are  
20 discussed in detail in Schnell, USP 3,028,365; Glass, USP 4,529,791; and Grigo, USP 4,677,162.

#### Use of a Polyester as the Blending or Molding Polymer.

When a polyester is used as a blending or molding polymer in the  
25 blend compositions of this invention, the polyester will be as described above as subcomponent (c) with respect to preparation of the branched block ethylene polymer. It is preferred that a polyester used as the blending or molding polymer in the blend compositions of this invention have an intrinsic viscosity of  
30 about 0.85 or more, advantageously about 0.9 to about 1.2, and preferably about 0.95 to about 1.05.

It is further preferred that when a polyester is used both as subcomponent (c) of the branched block ethylene polymer and as the blending or molding polymer, a different polyester be used  
35 for each.

trimethylphenol (wherein each  $Q_1$  and one  $Q_2$  is methyl and the other  $Q_2$  is hydrogen). A variety of catalyst systems are known for the preparation of poly(phenylene ether)s by oxidative coupling. For the most part, they contain at least one heavy metal compound such as a  
5 copper, manganese or cobalt compound, usually in combination with various other materials. A first class of preferred catalyst systems consists of those containing a copper compound, such as are disclosed, for example, in U.S. Pat. Nos. 3,306,874, 3,306,875, 3,914,266 and 4,028,341. They are usually combinations of cuprous or cupric ions,  
10 halide (i.e., chloride, bromide or iodide) ions and at least one amine. Catalyst systems containing manganese compounds constitute a second preferred class. They are generally alkaline systems in which divalent manganese is combined with such anions as halide, alkoxide or phenoxide. Most often, the manganese is present as a complex with one  
15 or more complexing and/or chelating agents such as dialkylamines, alkanolamines, alkylenediamines, o-hydroxyaromatic aldehydes, o-hydroxyazo compounds, w-hydroxyoximes (monomeric and polymeric), o-hydroxyaryl oximes and  $\beta$ -diketones. Also useful are known cobalt-containing catalyst systems.

20

Poly(phenylene ether)s, as described above, are discussed in greater detail in U.S. Pat. No. 4,866,130.

Also included in the category of poly(phenylene ether)s is a  
25 poly(phenylene ether) blend which is prepared by blending a poly(phenylene ether) with polystyrene, a vinyl aromatic copolymer, and/or with other non-styrenic polymers as specified below. When the thermoplastic polymer used as a blending or molding polymer is a poly(phenylene ether) blend, such blend will be made up of about 20 to  
30 about 99 parts poly(phenylene ether), preferably about 30 to 90 parts poly(phenylene ether), by weight, with the balance being made up of polystyrene, a vinyl aromatic copolymer, and/or the non-styrenic polymers. A preferred such formulation contains about 30 to about 85 weight parts poly(phenylene ether), about 15 to about 70 weight parts  
35 selected from one or more of the following: polystyrene, high impact

homopolymers are those containing, for example, 2,6-dimethyl-1,4-phenylene ether units. Suitable copolymers include random copolymers containing such units in combination with, for example, 2,3,6-trimethyl-1,4-phenylene ether units.

5

Also included are poly(phenylene ether) containing moieties which modify properties such as molecular weight, melt viscosity and/or impact strength. Such polymers may be prepared by copolymerizing with or grafting onto the poly(phenylene ether), in known manner, such  
10 vinyl monomers as vinyl nitrile compounds (e.g. acrylonitrile) and vinyl aromatic compounds (e.g., styrene), or such polymers as polystyrenes and elastomers. The product typically contains both grafted and ungrafted moieties. Other suitable polymers are the coupled poly(phenylene ether)s in which the coupling agent is reacted,  
15 in known manner, with the hydroxy groups of two poly(phenylene ether) chains to produce a higher molecular weight polymer containing the reaction product of the hydroxy groups and the coupling agent. Illustrative coupling agents are low molecular weight polycarbonates, quinones, heterocycles, formals and poly(phenylene sulfide)s. For  
20 example, poly(phenylene ether)/polycarbonate copolymers are known and are discussed in U.S. Pat. No. 5,010,143.

The poly(phenylene ether) typically has a number average molecular weight within the range of about 3,000-40,000, and a weight  
25 average molecular weight within the range of about 20,000-80,000, as determined by gel permeation chromatography. Its intrinsic viscosity is typically in the range of about 0.15-0.6, and preferably at least 0.25, dL/g, as measured in chloroform at 25°C. However, values outside these ranges are permitted as well.

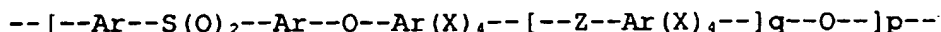
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The poly(phenylene ether)s are typically prepared by the oxidative coupling of at least one corresponding monohydroxyaromatic compound. Particularly useful and readily available  
monohydroxyaromatic compounds are 2,6-xyleneol (wherein each Q<sub>1</sub> is  
35 methyl and each Q<sub>2</sub> is hydrogen), whereupon the polymer may be characterized as a poly(2,6-dimethyl-1,4-phenylene ether), and 2,3,6-

Another variety of polysulfone is synthesized from a bisphenol which itself contains a sulfone bridge ("Bisphenol-S"). This polymerization is run at a higher temperature (up to about 285°C), in a dipolar aprotic solvent such as diphenyl sulfone and employs a base  
 5 such as sodium or potassium carbonate. Removal of water is typically not a concern. This type of polymer is available from ICI Americas, Inc. as Victrex™ polysulfone.

Other bisphenols which have been used to prepare polysulfone are  
 10 4,4'-dihydroxydiphenyl sulfide, 4,4'-dihydroxydiphenyl oxide, 4,4'-dihydroxydiphenylmethane, hydroquinone, bis(4-hydroxydiphenyl)-2,2-perfluoropropane, bis(4-hydroxydiphenyl)-1,1-cyclohexane, 4,4'-dihydroxybenzophenone, and 4,4'-dihydroxydiphenyl.

15 In general, the repeating unit of a polysulfone may be represented generally by structure as follows:



20 where Ar, D and E are as set forth above, q is about 0 to about 3 and p is about 10 to about 100.

Use of Polyimide or Polyetherimide as the Blending or Molding Polymer. A polyimide is a condensation polymer derived  
 25 from a bifunctional carboxylic acid anhydride and a primary diamine. Two equivalents of water are liberated by formation of the imide bond, one in the formation of the anhydride ring and the second as a result of displacement of oxygen in the ring by nitrogen. The polymer can alternatively be prepared by reaction  
 30 of a diamine directly with a tetracarboxylic acid. In either event, an intermediate is obtained, for example polyamic acid when the starting material is an anhydride, and the second equivalent of water is liberated by heating to form polymer. Reaction of a dianhydride and a diamine to form the polyamic acid  
 35 intermediate occurs at ambient temperatures in a dipolar aprotic solvent such as dimethylacetamide, cresol or o-chlorophenol.

polystyrene, styrene/butadiene/styrene and/or styrene/ethylene-butylene/styrene block terpolymer.

Use of Polysulfones as the Blending or Molding Polymer.

- 5 Polysulfones useful as the thermoplastic polymer in general may be described as polymers containing aromatic rings which are para-linked partly by sulfone groups and partly by dissimilar groups such as an ether or alkyl group or a single bond. A polysulfone does not, however, contain the carbonate [-C(O)-]  
10 linkage. A polysulfone is a clear, rigid thermoplastic with a glass transition temperature of about 180-250°C.

- A common variety of polysulfone is prepared by a nucleophilic substitution of 4,4'-dihalodiphenyl sulfone by Bisphenol-A in a  
15 dipolar aprotic solvent such as dimethyl sulfoxide or 1-methyl-2-pyrrolidinone. A fluoride or chloride may be used as the dihalide monomer. As in the production of polycarbonate, the bisphenol is activated to bisphenate form in a stoichiometric quantity of aqueous base such as sodium or potassium hydroxide. However, excess water is  
20 removed from the system by azeotropic distillation at 120-140°C before the bisphenate is contacted with the dihalo monomer.

- Polymerization is then carried out at 130-160°C under an inert atmosphere to prevent oxidation of the bisphenate salt. Molecular  
25 weight as high as 250,000 can be obtained in one hour, and monofunctional halides or phenols are consequently used as chain terminators to prevent the molecular weight of the polysulfone from becoming so high that it is too viscous for processing. The highest molecular weight of a Bisphenol-A polysulfone is obtained as the ratio  
30 of starting monomers approaches unity, and, for useful properties, that weight (expressed as reduced viscosity in chloroform at a concentration of 0.2g/100mL at 25°C) is usually at least 0.4 dL/g. Bisphenol-A polysulfone is available from Amoco Performance Products, Inc. as Udel™ polysulfone.

35

sulfone dianhydride, 1,2,5,6-naphthalenetetracarboxylic acid dianhydride, 2,2',3,3'-biphenyltetracarboxylic acid dianhydride, hydroquinone bisether dianhydride, bis(3,4-dicarboxyphenyl) sulfoxide dianhydride, and 3,4,9,10-perylene tetracarboxylic acid dianhydride.

5

Bisphenols useful for preparation of a polyetherimide include those described above in connection with the preparation of polycarbonate. Representative dinitrobisimides useful for preparation of a polyetherimide include 1,3-bis(4-nitrophthalimido)benzene, 1,4-  
10 bis(4-nitrophthalimido)benzene, 4,4'-bis(nitrophthalimido)diphenyl ether, 4,4'-bis(4-nitrophthalimido)diphenylmethane, 2,4-bis(4-nitrophthalimido)toluene, and 1,6-bis(4-nitrophthalimido)hexane.

15

Processes for Preparing Blends of the Branched Block Ethylene Polymers with the Blending or Modifying Polymer. Preparation of the compositions of this invention can be accomplished by any suitable mixing means known in the art. Typically the branched block ethylene polymer and the thermoplastic blending or molding polymer(s), and  
20 other components or additives which are optionally present in the compositions of this invention, are dry blended in a tumbler or shaker in powder or particulate form with sufficient agitation to obtain thorough distribution thereof. If desired, the dry-blended formulation can further be subjected to malaxation or to shearing  
25 stresses at a temperature sufficient to cause heat plastification, for example in an extruder with or without a vacuum. Other apparatus which can be used in the mixing process include, for example, a roller mill, a Henschel mixer, a ribbon blender, a Banbury mixer, or a reciprocating screw injection molding machine.

30

The method of preparation of a branched block ethylene polymer disclosed above lends itself to a preferred method of preparation of a blend of a branched ethylene polymer with a reactive thermoplastic polymer and optionally a blending or molding polymer. When using an extruder for preparation of a branched block ethylene polymer, the  
35 separate components from which it is prepared, and the blending polymer, are fed in sequence through separate ports during a single pass through one extruder for more convenient material handling.

Advancement to the final polymer is obtained by heating at 150-200°C for 3-5 hours to perform cyclodehydration. When an aromatic diamine is used, an accelerator such as triethylamine or acetic acid may be used in a solvent such as chlorobenzene.

5

A polyimide may also be prepared by reaction of aromatic dianhydrides with aromatic diisocyanates with the elimination of carbon dioxide, or by reaction of a bismaleimide with a diamine.

10

A polyetherimide may be prepared by a nucleophilic substitution reaction of a bisphenoxide salt with a dinitrobisimide, or by a polyimide-forming reaction as described above between a diamine and an ether-bridged dianhydride. The reaction between a bisphenoxide salt and a dinitrobisimide may be conducted in a dipolar aprotic solvent, such as dimethylformamide or dimethylsulfoxide in combination with toluene or chlorobenzene at about 40°C, or in N-methylpyrrolidinone with or without chlorobenzene at 80-130°C. A polyetherimide may also be prepared by displacement of chloro or fluoro groups on a bisimide.

15

20

Diamines useful for preparation of a polyimide may be aliphatic or aromatic and several useful varieties include m- and p-phenylenediamine, 2,4- and 2,6-diaminotoluene, p- and m-xylylenediamine, 4,4'-diaminobiphenyl, 4,4'-diaminodiphenyl ether, 4,4'-diaminobenzophenone, 4,4'-diaminophenyl sulfone, 4,4'-diaminodiphenyl sulfide, 4,4'-diaminodiphenylmethane, 3,3'-dimethylbenzidine, 4,4'-isopropylidenedianiline, 1,4-bis(p-aminophenoxy)benzene, 1,3-bis(p-aminophenoxy)benzene, hexa-, hepta-, nona-, and decamethylenediamines, 1,4-cyclohexanediamine, and bis(4-aminocyclohexyl)methane. Representative dianhydrides useful for

25

30

35

preparation of a polyimide include pyromellitic dianhydride, benzophenone dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 3,3',4,4'-biphenyltetracarboxylic acid dianhydride, bis(3,4-dicarboxyphenyl) ether dianhydride, bis(3,4-dicarboxyphenyl) thioether dianhydride, bisphenol A bisether dianhydride, 2,2-bis(3,4-dicarboxylphenyl)hexafluoropropane dianhydride, 2,3,6,7-naphthalenetetracarboxylic acid dianhydride, bis(3,4-dicarboxyphenyl)



Concerning the Incorporation of an Additional Supplemental Impact Modifier Into Blends of the Branched Block Ethylene Polymers with the Blending or Molding Polymer.

5        In a further embodiment of the invention, a blend of the branched block ethylene polymer with the blending or molding thermoplastic polymer may further include a supplemental impact modifier. Although the branched block ethylene polymer effectively serves as an impact modifier when present in a composition with a blending or molding  
10        polymer, better performance still may be attained in various situations by establishing a synergy in a composition between a branched block ethylene polymer and a supplemental impact modifier.

15        Appropriate supplemental impact modifiers include, for example, elastomers such as an A-B or A-B-A copolymer, a core-shell grafted copolymer or mixtures thereof.

20        An A-B or A-B-A copolymer useful as an impact modifier herein can be either linear, branched, radial or teleblock, and can be either a di-block ("A-B") copolymer, tri-block ("A-B-A") copolymer, or radial teleblock copolymer with or without tapered sections, i.e. portions of the polymer where the monomers alternate or are in random order close to the point of transition between the A and B blocks.

25        The A portion is frequently prepared by polymerizing one or more vinyl aromatic hydrocarbon monomers such as the various styrenic monomers and substituted varieties thereof; has a weight average molecular weight of about 4,000 to about 115,000; and has properties characteristic of thermoplastic substances in that it has the  
30        stability necessary for processing at elevated temperatures and yet possesses good strength below the temperature at which it softens. The B portion of the copolymer typically results from polymerizing substituted or unsubstituted C<sub>3</sub>-C<sub>10</sub> dienes, particularly conjugated dienes such as butadiene or isoprene; has a weight average molecular  
35        weight of about 20,000 to about 450,000; and is characterized by elastomeric properties which allow it to absorb and dissipate an applied stress and then regain its shape.

To reduce oxidative and thermal instability, the A-B or A-B-A

Materials which are added later in the sequence are typically fed through a downstream port in the extruder.

For example, an ethylene polymer may be fed first, followed next  
5 by an ethylenically unsaturated functionalized organic compound,  
followed then by a reactive thermoplastic polymer, and followed last  
by the blending or molding polymer. In the alternative, a previously  
prepared branched ethylene polymer may be fed first, followed next by  
a reactive thermoplastic polymer, followed last by the blending or  
10 molding polymer. In the alternative, a previously prepared branched  
ethylene polymer may be fed together with a reactive thermoplastic  
polymer, followed then by the blending or molding polymer.

Selection of the sequence in which the branched ethylene polymer  
15 reacts with the reactive thermoplastic polymer to form the branched  
block ethylene polymer before the blending or molding polymer is added  
to the mixer gives a product having superior properties compared to  
addition of the blending polymer before or simultaneously with the  
reactive thermoplastic polymer. Such a result is obtained because the  
20 presence of the blending or molding polymer may act as a physical  
barrier which hinders formation of the ethylenically unsaturated  
functionalized organic compound into a branch, or may hinder reaction  
of the reactive thermoplastic polymer with any such branched that are  
formed.

25 Preparation of Articles Comprising Blends fo the Branched Block  
Ethylene Polymer with the Blending or Molding Thermoplastic  
Polymer(s). When softened or melted by the application of heat and/or  
shear, the compositions of this invention are useful for fabrication  
30 and can be formed or molded using conventional techniques such as  
compression, injection molding, gas assisted injection molding,  
calendering, vacuum forming, thermoforming, extrusion and/or blow  
molding, alone or in combination. The compositions can also be  
formed, spun or drawn into films, fibers, multi-layer laminates or  
35 extruded sheets, or can be compounded with one or more organic or  
inorganic substances, on any machine suitable for such purpose.

acrylonitrile; a C1-C8 alkyl acrylate such as ethyl acrylate or hexyl acrylate; a C1-C8 alkyl methacrylate such as methyl methacrylate or hexyl methacrylate; glycidyl methacrylate; acrylic or methacrylic acid; and the like or a mixture of two or more thereof. The  
5 preferred grafting monomers include one or more of styrene, acrylonitrile and methyl methacrylate.

The grafting monomers may be added to the reaction mixture simultaneously or in sequence, and, when added in sequence, layers,  
10 shells or wart-like appendages can be built up around the substrate latex, or core. The monomers can be added in various ratios to each other although, when just two are used, they are frequently utilized in equal amounts. A typical weight ratio for methyl methacrylate/butadiene/styrene copolymer ("MBS" rubber) is about 60-80  
15 parts by weight substrate latex, about 10-20 parts by weight of each of the first and second monomer shells. A preferred formulation for an MBS rubber is one having a core built up from about 71 parts of butadiene, about 3 parts of styrene, about 4 parts of methyl methacrylate and about 1 part of divinyl benzene; a second phase of  
20 about 11 parts of styrene; and a shell phase of about 11 parts of methyl methacrylate and about 0.1 part of 1,3-butylene glycol dimethacrylate, where the parts are by weight of the total composition. A diene-based, core-shell graft copolymer elastomer and methods for making same, as described above, are discussed in greater  
25 detail in Saito, USP 3,287,443, Curfman, USP 3,657,391, and Fromuth, USP 4,180,494.

A core-shell grafted copolymer based on an alkyl acrylate rubber has a first phase forming an elastomeric core and a second phase  
30 forming a rigid thermoplastic phase about said elastomeric core. The elastomeric core is formed by emulsion or suspension polymerization of monomers which consist of at least about 50 weight percent alkyl and/or aralkyl acrylates having up to fifteen carbon atoms, and, although longer chains may be used, the alkyls are preferably C<sub>2</sub>-C<sub>6</sub>,  
35 most preferably butyl acrylate. The elastomeric core phase should have a T<sub>g</sub> of less than about 10°C, and preferably less than about -20°C. About 0.1 to 5 weight percent of (i) a cross-linking monomer which has a plurality of addition polymerizable reactive groups all of which polymerize at substantially the same rate, such as butylene

copolymers used herein can also desirably be hydrogenated to reduce the degree of unsaturation on the polymer chain and on the pendant aromatic rings.

- 5       The most preferred vinyl aromatic A-B or A-B-A copolymers are vinyl aromatic/conjugated diene block copolymers formed from styrene and butadiene or styrene and isoprene. When the styrene/butadiene copolymers are hydrogenated, they are frequently represented as  
10       styrene/(ethylene/butylene) copolymer in the di-block form, or as styrene/(ethylene/butylene)/styrene copolymer in the tri-block form. When the styrene/isoprene copolymers are hydrogenated, they are frequently represented as styrene/(ethylene/propylene) copolymer in the di-block form, or as styrene/(ethylene/propylene)/styrene  
15       copolymer in the tri-block form. Vinyl aromatic/diene A-B or A-B-A copolymers such as are described above are discussed in greater detail in Holden, USP 3,265,766, Haefele, USP 3,333,024, Wald, USP 3,595,942, and Witsiepe, USP 3,651,014, which are available commercially as the various Kraton elastomers from Shell Chemical Company.
- 20       Core-shell grafted copolymer elastomers suitable for use herein as a supplemental impact modifier are those which are based on either a diene rubber, an alkyl acrylate rubber, or on mixtures thereof, and have an elastomeric, or rubber, phase which is greater than about 45% or more of the copolymer by weight. A core-shell grafted copolymer  
25       based on a diene rubber contains a substrate latex, or core, which is made by polymerizing a diene, preferably a conjugated diene, or by copolymerizing a diene with a mono-olefin or a polar vinyl compound, such as styrene, acrylonitrile, or an alkyl ester of an unsaturated carboxylic acid such as methyl methacrylate. The substrate latex is  
30       typically made up of about 40-85% diene, preferably a conjugated diene, and about 15-60% of the mono-olefin or polar vinyl compound. The elastomeric core phase should have a glass transition temperature ("T<sub>g</sub>") of less than about 10°C, and preferably less than about -20°C. A mixture of ethylenically unsaturated monomers is then graft  
35       polymerized to the substrate latex. A variety of monomers may be used for this grafting purpose, of which the following are exemplary: vinyl compounds such as vinyl toluene or vinyl chloride; vinyl aromatics such as styrene, alpha-methyl styrene or halogenated styrene; acrylonitrile, methacrylonitrile or alpha-halogenated

chain, hydrocarbon backbone ("olefinic elastomers"), which may be prepared predominantly from various mono- or dialkenyl monomers and may be grafted with one or more styrenic monomers. Representative examples of a few olefinic elastomers which illustrate the variation  
5 in the known substances which would suffice for such purpose are as follows: butyl rubber; chlorinated polyethylene rubber; chlorosulfonated polyethylene rubber; an olefin polymer or copolymer such as ethylene/propylene copolymer, ethylene/styrene copolymer or ethylene/propylene/diene copolymer, which may be grafted with one or  
10 more styrenic monomers; neoprene rubber; nitrile rubber; polybutadiene and polyisoprene.

An example of a preferred olefinic elastomer is a copolymer prepared from (i) at least one olefin monomer such as ethylene,  
15 propylene, isopropylene, butylene or isobutylene, or at least one conjugated diene such as butadiene, and the like, or mixtures thereof; and (ii) an ethylenically unsaturated monomer carrying an epoxide group (for example, glycidyl methacrylate), and, optionally, (iii) an ethylenically unsaturated monomer which does not carry an epoxide  
20 group (for example, vinyl acetate).

When the supplemental impact modifier is employed, it will advantageously be present in an amount (in parts by weight of the total blend composition) of at least about 1 part, preferably at least  
25 about 5 parts, more preferably at least about 10 parts, and most preferably at least about 15 parts. The supplemental impact modifier will typically be present in an amount of not more than about 50 parts, advantageously not more than about 40 parts, preferably not more than about 30 parts, and more preferably not more than about 25  
30 parts.

When the supplemental impact modifier is employed in conjunction with blends of a thermoplastic (such as polycarbonate) with a branched block ethylene polymer having a polyester as the reactive  
35 thermoplastic polymer component (c), the supplemental impact modifier will be present in such blend in an amount (in parts by weight of the total blend composition) of at least about 0.1 parts, advantageously at least about 0.5 parts, preferably at least about 1 parts, and more preferably at least about 3 parts; and yet not more than about about

diacrylate, and (ii) a graft-linking monomer which has a plurality of addition polymerizable reactive groups some of which polymerize at substantially different rates than others, such as diallyl maleate, is typically polymerized as part of the elastomeric core.

5

The rigid thermoplastic phase of the acrylate rubber is formed on the surface of the elastomeric core using suspension or emulsion polymerization techniques. The monomers necessary to create this phase together with necessary initiators are added directly to the reaction mixture in which the elastomeric core is formed, and polymerization proceeds until the supply of monomers is substantially exhausted. Ethylenically unsaturated monomers such as glycidyl methacrylate, or an alkyl ester of an unsaturated carboxylic acid, for example a C<sub>1</sub>-C<sub>8</sub> alkyl acrylate like methyl acrylate, hydroxy ethyl acrylate or hexyl acrylate, or a C<sub>1</sub>-C<sub>8</sub> alkyl methacrylate such as methyl methacrylate or hexyl methacrylate, or mixtures of any of the foregoing, are some of the vinyl monomers which can be used for this purpose. Either thermal or redox initiator systems can be used. Because of the presence of the graft linking agents on the surface of the elastomeric core, a portion of the chains which make up the rigid thermoplastic phase are chemically bonded to the elastomeric core. It is preferred that there be at least about 20% bonding of the rigid thermoplastic phase to the elastomeric core.

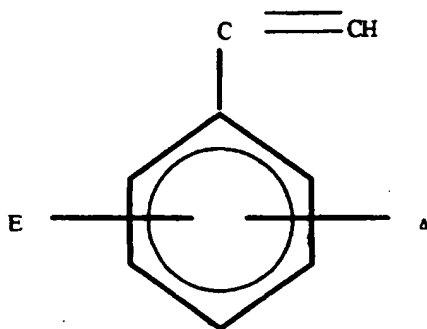
25

A preferred acrylate rubber is made up of more than about 45% to about 95% by weight of an elastomeric core and about 60% to about 5% of a rigid thermoplastic phase. The elastomeric core can be polymerized from about 75% to about 99.8% by weight C<sub>1</sub>-C<sub>8</sub> acrylate, preferably n-butyl acrylate. The rigid thermoplastic phase can be polymerized from at least 50% by weight of C<sub>1</sub>-C<sub>8</sub> alkyl methacrylate, preferably methyl methacrylate. Acrylate rubbers and methods for making same, as described above, are discussed in greater detail in Owens, USP 3,808,180 and Witman, USP 4,299,928. Various diene-based and acrylate-based core-shell grafted copolymers are available commercially from Rohm & Haas as the Acryloid™ or Paraloid™ elastomers.

30

35

Other supplemental impact modifiers or elastomers useful in the compositions of this invention are those based generally on a long-



25 parts, advantageously not more than about 20 parts, preferably not more than about 15 parts, and more preferably not more than about 10 parts.

5 Concerning the Use of a Styrenic Copolymer as an Additional Component of Blends of the Branched Block Ethylene Polymer with the Blending or Molding Thermoplastic Polymer.

10 In the embodiment of the invention which is a blend of the branched block ethylene polymer with a blending or molding thermoplastic polymer, such blend may further comprise a styrenic copolymer. Such styrenic copolymers have found particular utility in blends of the branched block ethylene polymer in which the reactive thermoplastic polymer is a polyester.

15

Suitable styrenic copolymers will be prepared from one or more styrenic monomers and one or more ethylenically unsaturated monomers copolymerizable with a styrenic monomer. The styrenic copolymer may be a random, alternate, block or grafted copolymer, and a mixture of  
20 more than one styrenic copolymer may be used as well.

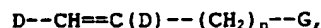
25 Styrenic monomers of particular interest for use in preparation of a styrenic copolymer, in addition to styrene itself, include one or more of the substituted styrenes or vinyl aromatic compounds described by the following formula [it being understood that a reference to "styrene" as a comonomer in component (c) is to be read as a reference to any of the styrenic or vinyl aromatic monomers described herein or any others of like kind]:



natural rubber, chlorinated rubber, 1,2-hexadiene, methyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-methyl-3-ethyl-1,3-butadiene, 2-ethyl-1,3-pentadiene, 1,3- and 2,4-hexadienes, chloro- and bromo-substituted butadienes such as dichlorobutadiene, 5 bromobutadiene, chloroprene and dibromobutadiene, and butadiene/isoprene and isoprene/isobutylene copolymers; 1,3-divinylbenzene; 2-phenyl propene; a C<sub>2</sub>-C<sub>10</sub> alkylene compound including halo-substituted derivatives thereof such as vinyl or vinylidene chloride; the alpha,beta-ethylenically unsaturated 10 carboxylic acids, such as acrylic acid, methacrylic acid, maleic acid, succinic acid, acotinic acid and itaconic acid, and their anhydrides and C<sub>1</sub>-C<sub>10</sub> alkyl, aminoalkyl and hydroxyalkyl esters and amides, such as alkyl acrylates and methacrylates such as methyl acrylate, propyl acrylate, butyl acrylate, octyl acrylate, methyl alpha-chloro 15 acrylate, methyl, ethyl or isobutyl methacrylate, hydroxyethyl and hydroxypropyl acrylates, aminoethyl acrylate and glycidyl methacrylate; maleic anhydride; an alkyl or aryl maleate or fumarate such as diethylchloromaleate or diethyl fumarate; an aliphatic or aromatic maleimide, such as N-phenyl maleimide, including the reaction 20 product of a C<sub>1</sub>-C<sub>10</sub> alkyl or C<sub>6</sub>-C<sub>14</sub> aryl primary amine and maleic anhydride; methacrylamide, acrylamide or N,N-diethyl acrylamide; vinyl ketones such as methyl vinyl ketone or methyl isopropenyl ketone; vinyl or allyl acetate and higher alkyl or aryl vinyl or allyl esters; vinyl alcohols; vinyl ethers such as C<sub>1</sub>-C<sub>6</sub> alkyl vinyl 25 ether and their alkyl-substituted halo derivatives; vinyl pyridines; vinyl furans; vinyl aldehydes such as acrolein or crotonaldehyde; vinyl carbazole; vinyl pyrrolidone; N-vinylphthalimide; and an oxazoline compound includes those of the general formula, where each J is independently hydrogen, halogen, a C<sub>1</sub>-C<sub>10</sub> alkyl radical or a C<sub>6</sub>-C<sub>14</sub> 30 aryl radical; and the like:

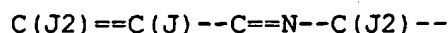
wherein each A is independently hydrogen, a C<sub>1</sub>-C<sub>6</sub> alkyl radical or a halogen atom such as chlorine or bromine; and each E is independently hydrogen, a C<sub>1</sub>-C<sub>10</sub> alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy radical, a halogen atom such as chlorine or bromine, or two E's may be joined to form a naphthalene structure. Representative examples of suitable styrenic monomers, in addition to styrene itself, include one or more of the following: ring-substituted alkyl styrenes, e.g. vinyl toluene, o-ethylstyrene, p-ethylstyrene, ar-(t-butyl)styrene, 2,4-dimethylstyrene; ring-substituted halostyrenes, e.g., o-chlorostyrene, p-chlorostyrene, o-bromostyrene, 2,4-dichlorostyrene; ring-alkyl, ring-halo-substituted styrenes, e.g. 2-chloro-4-methylstyrene and 2,6-dichloro-4-methylstyrene; ar-methoxy styrene, vinyl naphthalene or anthracene, p-diisopropenylbenzene, divinylbenzene, vinylxylene, alpha-methylstyrene, and alpha-methylvinyltoluene.

Ethylenically unsaturated monomers of particular interest for copolymerization with a styrenic monomer include one or more of those described by the formula:



wherein each D independently represents a substituent selected from the group consisting of hydrogen, halogen (such as fluorine, chlorine or bromine), C<sub>1</sub>-C<sub>6</sub> alkyl or alkoxy, or taken together represent an anhydride linkage; G is hydrogen, vinyl, C<sub>1</sub>-C<sub>12</sub> alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkaryl, arylalkyl, alkoxy, aryloxy, ketoxy, halogen (such as fluorine, chlorine or bromine), cyano or pyridyl; and n is 0-9.

Representative examples of ethylenically unsaturated monomers copolymerizable with a styrenic monomer are those which bear a polar or electronegative group and include one or more of the following: a vinyl nitrile compound such as acrylonitrile, methacrylonitrile, ethacrylonitrile, alphachloroacrylonitrile and fumaronitrile; a diene such as butadiene, isoprene, isobutylene, piperylene, cyclopentadiene,



Examples of preferred styrenic copolymers are vinyl aromatic/vinyl nitrile copolymers such as styrene/acrylonitrile  
 5 copolymer ("SAN"), styrene/maleic anhydride copolymer, styrene/glycidyl methacrylate copolymer, aryl maleimide/vinyl nitrile/diene/styrenic copolymer, styrene/alkyl methacrylate copolymer, styrene/alkyl methacrylate/glycidyl methacrylate copolymer, styrene/butyl acrylate copolymer, methyl  
 10 methacrylate/acrylonitrile/butadiene/styrene copolymer, or a rubber-modified vinyl aromatic/vinyl nitrile copolymer such as an ABS, AES or ASA copolymer.

ABS (acrylonitrile/butadiene/styrene copolymer) is an  
 15 elastomeric-thermoplastic composite in which vinyl aromatic/vinyl nitrile copolymer is grafted onto a polybutadiene substrate latex. The polybutadiene forms particles of rubber - the rubber modifier or elastomeric component - which are dispersed as a discrete phase in a thermoplastic matrix formed by random vinyl aromatic/vinyl nitrile  
 20 copolymer. Typically, vinyl aromatic/vinyl nitrile copolymer is both occluded in and grafted to the particles of rubber. AES (acrylonitrile/EPDM/styrene) copolymer is a styrenic copolymer which is obtained when vinyl aromatic/vinyl nitrile copolymer is rubber-modified by grafting vinyl aromatic/vinyl nitrile copolymer to a  
 25 substrate made up of an EPDM (ethylene/propylene/non-conjugated diene) rubber. AES copolymers are discussed in greater detail in Henton, USP 4,766,175. A vinyl aromatic/vinyl nitrile copolymer can also be crosslinked to an alkyl acrylate elastomer to form a rubber-modified styrenic copolymer, as in the case of an ASA  
 30 (acrylonitrile/styrene/acrylate) copolymer, which is discussed in greater detail in Yu, USP 3,944,631.

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invention. Preferably, however, the melt flow viscosity of the styrenic copolymer as determined by ASTM D-1238-65T(1) is from about 0.01 to about 10, more preferably from about 0.1 to about 5, and most preferably from about 2 to about 3, deciliters per minute. When  
5 the ethylenically unsaturated monomer possesses a polar group, the polar group typically has a group moment of about 1.4 to 4.4 Debye units, although values outside such ranges are permitted as well. A styrenic copolymer may be made by an emulsion, suspension or mass (bulk) method.

10

Methods for making ABS or other styrenic copolymers, as described above, are discussed in greater detail in Childers, USP 2,820,773, Calvert, USP 3,238,275, Carrock, USP 3,515,692, Ackerman, USP 4,151,128, Kruse, USP 4,187,260, Simon, USP 4,252,911 Weber, USP  
15 4,526,926, Rudd, USP 4,163,762 and Weber, USP 4,624,986.

The styrenic copolymer (when present) in the blends of the blending or molding thermoplastic polymer and the branched block ethylene polymer, will be present in an amount (in parts by weight  
20 based on the total weight of the blend composition) of at least about 5 parts, advantageously at least about 10 parts, preferably at least about 15 parts, and more preferably at least about 20 parts, and yet not more than about 75 parts, advantageously not more than about 55 parts, preferably not more than about 50 parts, and more preferably  
25 not more than about 45 parts.

Concerning the Presence of a Flow Modifier to Blends of the  
Branched Block Ethylene Polymer with a Blending or Molding  
Thermoplastic Polymer.

30 Blends of the branched block ethylene polymer with a blending or molding thermoplastic polymer may advantageously further include a flow modifier. Exemplary flow modifiers are polyamides and/or polyolefins.

The monomers copolymerized to form a styrenic copolymer may each be used in virtually any amount from 1 to 99 weight percent, but a styrenic copolymer will typically contain at least about 15 percent by weight, preferably at least about 35 percent by weight, and more preferably at least about 60 percent by weight of a styrenic monomer, with the balance being made up of one or more copolymerizable ethylenically unsaturated monomers. When rubber-modified, a styrenic copolymer will typically contain at least about 15 percent by weight, preferably at least about 25 percent by weight, and more preferably at least about 35 percent by weight of a styrenic monomer, with the balance being made up of one or more copolymerizable ethylenically unsaturated monomers.

The elastomeric phase of a rubber-modified styrenic copolymer as employed in the compositions of this invention is up to about 45 percent, preferably about 5 to 40 percent, more preferably about 10 to 35 percent, by weight of the copolymer. The preferred elastomeric phase exhibits a glass transition temperature ( $T_g$ ) generally less than  $0^{\circ}\text{C}$ , more preferably less than  $-30^{\circ}\text{C}$ , and most preferably from about  $-110^{\circ}\text{C}$  to about  $-50^{\circ}\text{C}$  as determined by ASTM D-746-52T or -56T. The elastomeric phase advantageously has an average particle size of about 10 microns or less, preferably in the range from about 0.05 to about 5 microns, and more preferably in the range from about 0.1 to about 0.3 microns, and typically exhibits an intrinsic viscosity, as determined at  $25^{\circ}\text{C}$  in toluene, of about 0.1 to about 5. In addition to the aforementioned monomeric components, the elastomeric phase may also contain relatively small amounts, usually less than about 2 weight percent based on the rubber, of a crosslinking agent such as divinylbenzene, diallylmaleate, ethylene glycol dimethacrylate and the like provided that such crosslinking does not eliminate the desired elastomeric character of rubber.

The molecular weight of a styrenic copolymer is not particularly critical so long as its melt flow viscosity is such that it can be melt blended with the other components of the compositions of this

advantageously not more than about 98 parts, and preferably not more than about 95 parts;

- 5 (c) Styrenic Copolymer (when present): at least about 5 parts, advantageously at least about 10 parts, preferably at least about 15 parts, and more preferably at least about 20 parts, and yet not more than about about 75 parts, advantageously not more than about 55 parts, preferably not more than about 50 parts, and more preferably not more than about 45 parts;
- 10 (d) Supplemental Impact Modifier (when present): at least about 0.1 parts, advantageously at least about 0.5 parts, preferably at least about 1 parts, and more preferably at least about 3 parts, and yet not more than about about 25 parts, advantageously not more than about 20 parts, preferably not more than about 15 parts, and more preferably not more than about 10 parts; and
- 15 (e) Flow Modifier Resin (when present): at least about 5 parts, advantageously at least about 10 parts, preferably at least about 15 parts, and more preferably at least about 20 parts, and yet not more than about about 75 parts, advantageously not more than about 55 parts, preferably not more than about 50 parts,
- 20 and more preferably not more than about 45 parts.

Particular Embodiment Wherein the Reactive Thermoplastic Polymer is a Polycaprolactone.

- 25 In one particular embodiment of the invention, branched block ethylene polymer will comprise a branched block ethylene polymer, wherein the reactive thermoplastic polymer is a polycaprylactone. Such compositions will find utility in combination with polycarbonate and a homogeneous ethylene polymer as the blending or molding polymers and a styrene-acrylonitrile grafted ethylene-propylene-diene rubber as the supplemental impact modifier. Such blends will comprise from
- 30 0.001 - 50 weight percent of the branched block ethylene polymer, 0.01 - 50 weight percent of the homogeneous ethylene polymer, 50-99.99

Polyamides useful as flow modifiers are as described above with respect to amine-functionalized polymers useful as the reactive thermoplastic polymer of subcomponent (c) of the branched block ethylene polymers of the invention. Polyolefins useful as flow  
5 modifiers are as described above with respect to possible compositions of the thermoplastic blending or molding polymer.

The flow modifier resin (when present) in the blends of the blending or molding thermoplastic polymer and the branched block  
10 ethylene polymer, will be present in an amount (in parts by weight based on the total weight of the blend composition) of at least about 5 parts, advantageously at least about 10 parts, preferably at least about 15 parts, and more preferably at least about 20 parts. Likewise, the flow modifier resin will be present in an amount of not  
15 more than about 75 parts, advantageously not more than about 55 parts, preferably not more than about 50 parts, and more preferably not more than about 45 parts.

Preferred Compositions Utilizing Branched Block Ethylene  
20 Polymers in Which the Reaction Thermoplastic Polymer of Subcomponent (c) is a Polyester:

Preferred compositions utilizing branched block ethylene polymers in which the reaction thermoplastic polymer of subcomponent  
25 (c) is a polyester will comprise the following:

- (a) Branched Block Ethylene Polymer: at least about 1 parts, advantageously at least about 2 parts, and preferably at least about 5 parts, and yet not more than about 40 parts,  
30 advantageously not more than about 30 parts, and preferably not more than about 20 parts;
- (b) Thermoplastic Blend or Molding Polymer: at least about 60 parts, advantageously at least about 70 parts, and preferably at least about 80 parts, and yet not more than about 99 parts,



acid; alumina trihydrate; ammonium fluoroborate; molybdenum oxide; halogenated hydrocarbons such as hexabromocyclodecane; decabromodiphenyl oxide; 1,2-bis(2,4,6-tribromophenoxy) ethane; halogenated carbonate oligomers such as those prepared from  
5 tetrabromobisphenol-A; halogenated epoxy resins such as brominated glycidyl ethers; tetrabromo phthalic anhydride; fluorinated olefin polymers or copolymers such as poly(tetrafluoroethylene); octabromodiphenyl oxide; ammonium bromide; isopropyl di(4-amino benzoyl) isostearoyl titanate; and metal salts of aromatic sulfur  
10 compounds such as sulfates, bisulfates, sulfonates, sulfonamides and sulfimides; other alkali metal and alkaline earth metal salts of sulfur, phosphorus and nitrogen compounds; and others as set forth in Laughner, USP 4,786,686; and the like, and mixtures thereof. A preferred flame retardant additive is antimony trioxide ( $\text{Sb}_2\text{O}_3$ ). When  
15 a flame retardant is used in the compositions of this invention, it is typically used in an amount of up to about 15 percent, advantageously from about 0.01 to 15 percent, preferably from about 0.1 to 10 percent and more preferably from about 0.5 to 5 percent, by weight of the total composition.

20

A variety of additives are optionally advantageously used in the compositions of this invention for other purposes such as the following: antimicrobial agents such as organometallics, isothiazolones, organosulfurs and mercaptans; antioxidants such as  
25 phenolics, secondary amines, phosphites and thioesters; antistatic agents such as quaternary ammonium compounds, amines, and ethoxylated, propoxylated or glycerol compounds; fillers and reinforcing agents such as talc, clay, mica, silica, quartz, kaolin, aluminum nitride,  $\text{TiO}_2$ , calcium sulfate,  $\text{B}_2\text{O}_3$ , alumina, glass flakes, beads, whiskers or  
30 filaments, nickel powder and metal or graphite fibers; hydrolytic stabilizers; lubricants such as fatty acids, fatty alcohols, esters, fatty amides, metallic stearates, paraffinic and microcrystalline waxes, silicones and orthophosphoric acid esters; mold release agents such as fine-particle or powdered solids, soaps, waxes, silicones,  
35 polyglycols and complex esters such as trimethylolpropane tristearate or pentaerythritol tetrastearate; pigments, dyes and colorants;

weight percent polycarbonate, and 0.001 - 10 weight percent of the styrene-acrylonitrile grafted ethylene-propylene-diene rubber.

Such compositions have good melt processability and toughness, making them useful for profile extrusion, injection molding  
5 applicaitons for automotive applications, computer and business equipment, communication devices, and other thin wall injection molding applications.

Concerning the Presence of Additives to the Branched Block Ethylene  
Polymers and/or to the Blends of the Branched Block Ethylene Polymers  
10 with an Additional Blending or Molding Polymer:

A variety of additives are optionally advantageously employed to promote flame retardance or ignition resistance in the compositions of this invention. Representative examples thereof include the oxides  
15 and halides of the metals of Groups IVA and VA of the periodic table such as the oxides and halides of antimony, bismuth, arsenic, tin and lead such as antimony oxide, antimony chloride, antimony oxychloride, stannic oxide, stannic chloride and arsenous oxide; the organic and inorganic compounds of phosphorous, nitrogen, boron and sulfur such as  
20 aromatic phosphates and phosphonates (including halogenated derivatives thereof), alkyl acid phosphates, tributoxyethyl phosphate, 1,3-dichloro-2-propanol phosphate, 3,9-tribromoneopentoxo-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-dioxide, phosphine oxides, ammonium phosphate, zinc borate, thiourea, urea, ammonium  
25 sulfamate, ammonium polyphosphoric acid and stannic sulfide; the oxides, halides and hydrates of other metals such as titanium, vanadium, chromium and magnesium such as titanium dioxide, chromic bromide, zirconium oxide, ammonium molybdate and stannous oxide hydrate; antimony compounds such as antimony phosphate, sodium  
30 antimonate,  $\text{KSb(OH)}_6$ ,  $\text{NH}_4\text{SbF}_6$  and  $\text{SbS}_3$ ; antimonate esters of inorganic acids, cyclic alkyl antimonate esters and aryl antimonate acid compounds such as potassium antimony tartrate, the antimony salt of caproic acid,  $\text{Sb(OCH}_2\text{CH}_3)_3$ ,  $\text{Sb[OCH(CH}_3\text{)CH}_2\text{CH}_3\text{]}_3$ , antimony polyethylene glycorate, pentaerythritol antimonate and triphenyl antimony; boric

preferably at least about 1 and even more preferably at least about 10 percent by weight.

#### Examples

5

The following examples are offered to illustrate but not limit the invention. Percentages, ratios and parts are by weight unless stated otherwise. Examples of the invention (Ex.) are designated numerically, while comparative samples (C.S.), which are not examples of the invention, are designated alphabetically.

10

To illustrate the practice of this invention, examples of several preferred embodiments are set forth below, however, these examples are not meant in any manner to restrict the scope of this invention. Some of the particularly desirable features of this invention may be seen by contrasting the characteristics of the Examples with those of various controlled formulations (Comparative Samples) which do not possess the features of, and are not therefore embodiments of, this invention.

20

Unless indicated otherwise, for Examples 1-7, the branched block ethylene polymer contained in the compositions of the Examples is prepared by dry blending Nylon 6 (having a weight average molecular weight of 22,000 and a melt index of 7), and a linear or substantially linear ethylene polymer (containing a 1 weight percent maleic anhydride branch) in amounts, respectively, as shown below. The maleic anhydride branch is formed on the linear or substantially linear ethylene polymer in an amount of 1 weight percent, based on the weight of the branched linear or substantially linear ethylene polymer, using a peroxide initiator. The dry blend of Nylon 6 and branched linear or substantially linear ethylene polymer is then melt mixed in a 30 mm Werner & Pfleiderer extruder to cause the Nylon 6 to react with the maleic anhydride branch and add as the final block to form a branched block ethylene polymer. Conditions used in such reactive extrusion are: zone temperatures of 150, 200, 250, 250 and 250°C; 250 rpm; 70-85 percent torque; and a 30 second residence time.

35

plasticizers such as esters of dibasic acids (or their anhydrides) with monohydric alcohols such as o-phthalates, adipates and benzoates; heat stabilizers such as organotin mercaptides, an octyl ester of thioglycolic acid and a barium or cadmium carboxyalte; ultraviolet  
5 light stabilizers such as a hindered amine, an o-hydroxy-phenylbenzotriazole, a 2-hydroxy,4-alkoxybenzophenone, a salicylate, a cyanoacrylate, a nickel chelate and a benzylidene malonate and oxalanilide. A preferred hindered phenolic antioxidant is Irganox™ 1076 antioxidant, available from Ciba-Geigy Corp. Such additives, if  
10 used, typically do not exceed 45 percent by weight of the total composition, and are advantageously from about 0.001 to 15 percent, preferably from about 0.01 to 10 percent and more preferably from about 0.1 to 10 percent, by weight of the total composition.

15 In the case of blends of the branched block ethylene polymers with an additional modifying or blending polymer, the polymer blend may likewise optionally include other additives, such as fillers, colorants, antioxidants, antistats, slip agents, tackifiers, fragrances, and the like.

20

Concerning the Use of the Branched Block Ethylene Polymers to Enhance Service Temperature. The branched block ethylene polymers of the invention have a relatively softer segment of ethylene polymer and a relatively harder segment of reactive thermoplastic polymer, which  
25 will preferably be an engineering thermoplastic. The presence of the harder engineering thermoplastic segment serves to extend the upper service temperature of the ethylene polymer. In this embodiment, the engineering thermoplastic impact modifiers are preferably present in amounts less than about 50, more preferably less than about 40, most  
30 preferably less than about 30, even more preferably less than about 20 percent by weight based on total weight of the branched block ethylene polymer of the invention. At these amounts, the engineering thermoplastic is observed to extend the range of temperatures in which the branched block ethylene polymer is serviceable (does not melt or  
35 deform undesirably). The amount of ethylene copolymer is preferably at least about 0.01, more preferably at least about 0.1, most

"EP" is the weight percent of linear or substantially linear ethylene polymer present in the blended composition, whether the ethylene polymer is unbranched, branched or formed into a branched block ethylene polymer.

Nylon 6 is a 7 melt index, 22,000 molecular weight polyamide (Capron 8207) commercially available from Allied Signal.

EG8200gMAH - A polyolefin elastomer having an  $I_2$  of 5 g/10 min. grafted with 1 wt. % maleic anhydride

ENGAGE\* 8150 - A polyolefin elastomer having an  $I_2$  of 0.5 g/10 min., commercially available from The Dow Chemical Company.

The following tests of physical and mechanical properties are performed on Examples 1-5 and Controls A-C, and the results of these tests are also shown in Table I:

Impact resistance ("Izod") is measured by the Izod test according to ASTM Designation D 256-84 (Method A) at 25°C. The notch is 10 mils (0.254 mm) in radius. Izod results are reported in ft-lb/in.

Impact resistance ("Weldline") is also measured by the Izod test according to ASTM Designation D 256-84 (Method A) at 25°C, but with respect to a sample which is formed with a butt weld in a double gated mold. The sample is unnotched, and it is placed in the vise so that the weld is 1 mm above the top surface of the vise jaws. Weldline results are also reported in ft-lb/in, except as to Example 5 where "N.B." indicates that the sample did not break.

The dart drop impact test ("Dart Drop") is performed at 23°C by dropping a 100 pound weight which carries a ½" dart onto a circular test sample which is 1/8" thick. The weighted dart falls freely on a slotted track and impacts the sample, which is secured in position in the path of descent on an aluminum cast base with a 0.640 inch hole to

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\* Trademark of The Dow Chemical Company

The branched block ethylene polymer is passed through an ice water bath, chopped into granules and collected for blending with a polyolefin resin.

- 5 Blend compositions are prepared by mixing the dry components of each on a paint shaker for 5 minutes, and then feeding the dry-blended formulation to the Werner & Pfleiderer extruder under the same conditions used to prepare the branched block ethylene polymer, except that the zone temperatures are 150, 200, 280, 280 and 280°C. The  
10 extrudate is again cooled in the form of strands and comminuted as pellets. The pellets are dried in an air draft oven for 3 hours at 120°C, and are then used to prepare test specimens on a 70 ton Arburg molding machine on which the barrel temperature is 200°C (feed), 250°C, 250°C and 255°C (nozzel), the mold temperature is 80°F, and the  
15 screw speed is 120 rpm.

"Polypropylene" is Profax™ 6323 polypropylene from Himont;

- "HDPE" is high density polyethylene having a density of about  
20 0.96 g/cm<sup>3</sup> and an I<sub>2</sub> melt index (according to ASTM D 1238) of about 10 g/10 min.;

"POE" is an unbranched substantially linear ethylene polymer, as described above;

- 25 "POE-b-MAH" is a substantially linear ethylene polymer containing a maleic anhydride branch, as described above;

- "B/BEP I" is a branched block ethylene polymer prepared from 70 weight percent substantially linear ethylene polymer containing a  
30 maleic anhydride branch and 30 weight percent Nylon 6;

- "B/BEP II" is a branched block ethylene polymer prepared from  
(i) 80 weight percent Tafmer™ P-0180 ethylene/propylene copolymer, a linear homogeneous ethylene polymer from Mitsui Petrochemical which  
35 has a density of 0.869 g/cm<sup>3</sup>, a melt index (I<sub>2</sub>) of 4 and a maleic anhydride branch; and (ii) 20 weight percent Nylon 6; and

## SPECIFIC EMBODIMENTS

## Sample Preparation

5 All samples were prepared by feeding polymer into a Werner-Pfleiderer ZSK-53/5L co-rotating twin screw extruder. After the polymer was fed into the extruder, a mixture of maleic anhydride (MAH)/methyl ethyl ketone (MEK)/LUPERSOL 130 (Initiator) at a weight ratio of 1:1:0.032, respectively, was fed into the end of Zone 1 of the extruder through an injection nozzle by a metering pump. LUPERSOL 10 130 is 2,5-di(t-butyl peroxy)hexyne-3 manufactured and sold by Atochem. The extruder was maintained at a vacuum level of greater than or equal to 26 inches of mercury to facilitate devolatilization of solvent, unreacted MAH and other contaminants.

Attane® resin is a ULDPE ethylene/1-octene resin manufactured and sold by The Dow Chemical Company. Dowlex® resin is a LLDPE 15 ethylene/1-octene resin manufactured and sold by The Dow Chemical Company. Tafmer® P-0180 resin is an ethylene/propylene copolymer resin manufactured and sold by Mitsui Petrochemical.

20 The following materials are used:

ADMER QF 500A, a polypropylene grafted with 1.5 wt % MAH and manufactured and sold by Mitsui Petrochemical; the grafted polymer had a melt index of 3.0 g/10 min. at 230 C and a density of 0.900 g/cm<sup>3</sup>.

25 Primacor® 3460, a copolymer of ethylene and acrylic acid manufactured and sold by The Dow Chemical Company; this material contained 9.7 wt % acrylic acid monomer and had a melt index of 20 g/10 min.

30 Graft-modified homogeneous ethylene polymer; this material contained 1.3 wt % MAH, had a melt index of 0.25 g/10 min., and a density of 0.870 g/cm<sup>3</sup>.

Profax® 6524, a polypropylene manufactured and sold by Himont; 35 it had a melt index of 4 g/10 min. at 230 C and a density of 0.9 g/cm<sup>3</sup>.

accept the dart after it impacts the sample. The instrument is a Dynatup Model 8250. The sample fails if it shows a crack or perforation on the side on which impact did not occur. The results are either pass (no break or perforation by the dart at the point of impact) or fail (material exhibits crack or perforation) when the dart has developed a particular amount of energy by falling from the necessary height on the track, as indicated thereon, to develop such energy. The value recorded in Table I is either "pass" or the greatest amount of energy a sample could accept without failing, expressed in in-lb.

Deflection temperature under load ("D.T.U.L.") is measured in accordance with ASTM Designation D 648-82 at 66 psi. Results are reported in °C.

Flexural modulus ("F. Modulus") is determined according to ASTM D 790. Results are reported in psi.

Unless indicated to the contrary, the substantially linear ethylene polymers used in the examples are prepared in accordance with the techniques set forth in USP 5,272,236 via a solution polymerization process utilizing a  $[(CH_3)_4C_5)-(CH_3)_2 Si-N-(t-C_4H_9)]Ti(CH_3)_2$  organometallic catalyst activated with tris (perfluorophenyl)borane. Unless indicated to the contrary, all parts and percentages are by weight, total weight basis. Unless indicated to the contrary, the following test procedures are utilized:

- |                                      |   |
|--------------------------------------|---|
| 1. Notched IZOD Impact<br>(ft-lb/in) | ASTM D-256 (at 23 C, 0 C, -18 C, -29 C and -40 C)                           |
| 2. Tensile (psi)                     | ASTM D-638  |
| 3. Yield (psi)                       | ASTM D-638  |
| 4. Elongation (%)                    | ASTM D-638  |
| 5. Whiteness Index (WI)              | ASTM E-313  |
| 6. Yellowness Index (YI)             | ASTM E-313  |
| 7. Particle Size (microns)           | Electron micrographs of<br>microtomed molded test samples<br>ASTM D-3763-86 |
| 8. Dynatup                           | ASTM D-3763-86 (at -29 C)   |



Maleic anhydride grafted ethylene 1-octene copolymer (ITP-g-MAH) prepared by grafting maleic anhydride to ethylene-octene copolymer by reactive extrusion was used in this study. The ethylene-octene copolymer used to make the ITP-g-MAH was a copolymer made in solution polymerization process from a constrained geometry single site catalyst. The final graft copolymer (lot XUR-1567-48562-D4) had a melt index of approximately 0.5 g/10 min, density of 0.87 g/cc, and MAH content of 1 weight percent. (1%MAH-g-ITP).

Polybutyleneterephthalate (PBT) was Celanex 2002 from Celanese (0.9 IV)

Acrylic copolymer consisting of methylmethacrylate-butylacrylate-glycidyl methacrylate (MMA/GMA), 90:8:2 ratio by weight.

#### Test Methods:

The dynamic mechanical properties of the samples were studied using Rheometrics Solid analyzer RSA-II. The test sample were prepared in the form of thin films (about 15-20 mil thickness). The sample was measured over a range temperature range from -120°C to highest possible temperature at which the sample either melted or deformed excessively. The measurement were conducted at the frequency of 10 rad/s and at  $7.0 \times 10^{-4}$  strain.

Tensile properties were tested on an Instron Series IX Automated Testing System 1.04. Machine parameters of test are: Sample rate 18.21 pts/sec; Crosshead speed: 2.00 in/min; Full Scale Load Range: 10.00(lbs); Humidity: 50%; Temperature: 73°F.

#### Example 1

The composition was produced by dry blending/mixing ITP-g-MAH (1400 g) and PBT (600 g) and subsequently melt blending using a 30 mm Werner & Pfleiderer twin screw extruder (250 RPM, feed rate to give 70-85% torque, and five barrel zone temperatures set at 150, 200, 250, 250, 250°C). Extrudate was pelletized using a Conair strand chopper. The results in Figure 1 indicate that MAH-g-ITP/PBT blend has higher service temperature than control samples, ITP-g-MAH or ITP/PBT blend. Using dynamic mechanical analysis (solid state, extension), both

The graft-modified homogeneous ethylene polymer (referred to below as INSITE<sup>TM</sup> Technology polymer or ITP) was prepared according to the procedure described in USP 4,950,541. The polymer components were  
5 dry mixed at a certain weight ratio, and were then fed into a Werner-Pfleiderer ZSK-30 twin-screw extruder operated at about 210 C. The blends were made in one extrusion pass.

Injection molded samples were prepared using a 50 ton Negri-  
10 Bossi Injection Molder operated with a barrel temperature between 200 and 250 C, a barrel pressure of 40 bars, cooling mold temperature of 85 F (29 C), and a residence time in the cooling mold of about 12 seconds. The samples were formed into 2.5" x 6.5" x 0.075" plaques.

15 The flex modulus and IZOD impact properties (at room temperature and -30 C) were measured for each of the samples in Table 8. These properties are important in many applications, e.g., automobile parts. The properties were measured according to ASTM D-790 and D-256, respectively.

20 Ethylene-propylene diene elastomer functionalized with maleic anhydride and sold by Uniroyal Chemical (Product designated - ROYALTUF 465A).

25 Ethylene-propylene elastomer functionalized with maleic anhydride and sold by Exxon Chemical (Product designated -Exxelor VA 1801).

30 An ethylene-propylene elastomer (Taifmer P-0180 from Mitsui) graft modified with maleic anhydride as described above.

Nylon 1000-1 is a low  $M_w$  Nylon 6,6 from Hoechst-Celanese used for injection molding

35 Nylon 1200-1 is a high  $M_w$  Nylon 6,6 from Hoechst-Celanese used for extrusion

granules and collected for final blending with the specified polyolefin matrix resin

5        Figures 4 and 5 graphically compare the rheological and Tan  
Delta properties at shear rates from 0.1 rads/sec to 100 rads/sec of a  
substantially linear ethylene elastomer, a maleic anhydride grafted  
substantially linear ethylene elastomer and a polyamide modified  
substantially linear ethylene elastomer. Figures 6 thru 9 (190°C &  
10       230°C) illustrate the effect of various concentrations of polyamide in  
maleic anhydride grafted substantially linear ethylene elastomers on  
these same rheological and elastic modulus properties. These figures  
illustrate the new nylon modified Engage elastomers possess not only a  
tremendous increase in shear sensitivity, but a significantly higher  
melt elasticity (lower Tan Delta) than a typical Engage\* polymer  
15       (exemplary of a narrow dispersity ethylene polymer). It is  
interesting to note that the slope of the viscosity curve at 190°C  
(below the melting point of Nylon 6) shows little change from the  
slope of the viscosity curve at 230°C (above the melting point of  
Nylon 6) just the expected shift due to higher temperatures.

20

control samples failed at about 60°C, while ITP-g-MAH/PBT was stable up to 120°C. The rheology comparison is shown in Figure 2. The results show that the ITP-g-MAH/PBT is a thermoplastic elastomer with improved processability and enhanced pseudo plastic ("shear thinning") behavior. As set forth in Figure 19, the ITP-g-MAH/PBT blend also has improved tensile properties compared to ITP alone. Tan delta data taken from DMS testing in Figure 2 & 3 also indicates these materials should be useful in blow molding and thermoforming applications.

#### Example 2

The composition was produced by mixing and melt blending ITP-g-MAH (133g) and MMA/GMA acrylic copolymer (57 g) in a Haake System 90 torque rheometer at 230°C for 10 minutes. The resulting mixture was subsequently cooled to ambient temperature and pelletized using a mill. The RSA results in Figure 4 indicate the reactive blend of ITP-g-MAH/(MMA/GMA) has high service temperature, i.e., the sample is stable up to 110°C.

Although this invention has been described in considerable detail through the preceding examples, such detail is for the purpose of illustration only and is not to be construed as a limitation upon the invention. Many variations can be made upon the preceding examples without departing from the spirit and scope of the invention as described in the following claims.

#### Examples 3-7

The nylon (exemplary of an engineering thermoplastic) modified elastomers explored during the course of this research are listed in Table 1. These compositions were prepared by dry blending the maleic anhydride grafted elastomers MAH modified Engage<sup>®</sup> 8200 (Trademark of The Dow Chemical Company) (EG 8200 MAH) with Nylon 6 at the specified ratios and melt mixed at 260°C on a 35mm Werner-Pfleiderer co-rotating, twin screw extruder at a speed of 250 rpm. Each extruded modified elastomer was passed through a ice water bath, chopped into

The branched block ethylene polymer contained in the compositions of Examples 8-24 is prepared by dry blending Nylon 6 (having a weight average molecular weight of 22,000 and a melt index of 7), and an ethylene polymer containing a maleic anhydride branch point ("E/MAH polymer") in amounts, respectively, as shown below. The maleic anhydride branch point is formed on the E/MAH polymer, using a peroxide initiator, in an amount of about 1 weight percent based on the weight of the E/MAH polymer. The dry blend of nylon 6 and the E/MAH polymer is then melt mixed in a 30 mm Werner & Pfleiderer extruder to cause the nylon 6 to react with the maleic anhydride branch point and add as the final block on the E/MAH copolymer to form a branched block ethylene polymer. Conditions used in such reactive extrusion are: zone temperatures of 150, 200, 250, 250 and 250°C; 250 rpm; 40-65 percent torque; and a 30 second residence time. The branched block ethylene polymer is passed through an ice water bath, chopped into granules and collected for blending with a thermoplastic molding polymer.

The final compositions of Examples 8-24 and Controls A-I are prepared by mixing the dry components of each on a paint shaker for 5 minutes, and then feeding the dry-blended formulation to the Werner & Pfleiderer extruder under the same conditions used to prepare the branched block ethylene polymer, except that the zone temperatures are 150, 200, 280, 280 and 280°C. The extrudate is again cooled in the form of strands and comminuted as pellets. The pellets are dried in an air draft oven for 3 hours at 120°C, and are then used to prepare test specimens on a 70 ton Arburg molding machine on which the barrel temperatures are 200°C (feed), 250°C, 250°C and 255°C (nozzle), the mold temperature is 80°F, and the screw speed is 120 rpm. Samples are not annealed before testing.

The formulation content of Examples 8-13 and of Controls A-D is given below in Table II, in parts by weight of the total composition.

In Table I:

"Polypropylene" is Profax\_ 6323 polypropylene from Himont having a melt index of about 12, one of the types of polyolefin resin described above as a blend component (b);

"HDPE" is high density polyethylene having a density of about

Table 1

Branched Block Ethylene Polymers wherein the Reactive Thermoplastic is  
Nylon 6

Example:	3	4	5	6	7
Engage* 8200 /MAH	1800	1700	1600	1500	1400
Nylon 6	200	300	400	500	600
weight percent nylon	10	15	20	25	30

5

\* Ethylene polymers commercially available from The Dow Chemical  
Company

10 Polymers of the invention whose characteristics are represented  
in Figures 4-18 are prepared as in Examples 3-7. The polymers of  
Figures 1-2a, 2b are prepared as those of Examples 1 and 2.

15 The tan delta value of the branched block ethylene polymer of  
this invention is also superior to that of either a homogeneous  
ethylene polymer or a branched homogeneous ethylene polymer, and is  
indicative of significantly high melt elasticity (high storage  
modulus) at low as well as at high shear. Moreover, it is found that  
the branched block ethylene polymer of this invention has the  
corresponding effect on a blend of a molding polymer therewith. Such  
20 a blended composition displays greater shear sensitivity and greater  
melt elasticity at low shear than a composition modified with just a  
homogeneous ethylene polymer or a branched homogeneous ethylene  
polymer.

25 Examples 8-24: Use of Branched Block Ethylene Polymers wherein the  
Reactive Thermoplastic Polymer of Subcomponent(c) is an Amine-  
Functionalized Polymer:

Table II  
Content of  
Examples 8-13 and Controls A-D

	Controls				Examples								
	A	B	C	D	8	9	10	11	12	13			
Polypropylene	2,000	1,500	1,500	1,500	1,600	1,500	1,400	1,500	1,500				
HDPE										1,600			
Ethylene Polymer		500		350				200					
E/NAH Copolymer			500										
Nylon 6				150									
Branched Block Ethylene Polymer I					400	500	600	300		400			
Branched Block Ethylene Polymer II									500				
Percent Ethylene Polymer	0	25	24.8	17.5	14.0	17.5	21.0	20.4	17.3	19.0			

0.96 g/cm<sup>3</sup> and an I2 melt index (according to ASTM D 1238) of about 35, another of the types of polyolefin resin described above as a blend component (b);

5 "Ethylene Polymer" is a "substantially linear" ethylene polymer, having a density of about 0.87 g/cm<sup>3</sup>, which does not contain a maleic anhydride branch point;

10 "E/MAH Copolymer" is a "substantially linear" ethylene polymer, having a density of about 0.87 g/cm<sup>3</sup>, containing maleic anhydride as a branch point in an amount of about 1.0 wt%;

15 "Nylon 6" is Capron\_ 8207 polyamide from Allied Signal, having a melt index of about 7, and a weight average molecular weight of about 22,000;

20 "Branched block ethylene polymer I" is a branched block ethylene polymer prepared from (i) 70 weight percent E/MAH copolymer having an I2 of about 0.5, in which the ethylene polymer is a "substantially linear"; and (ii) 30 weight percent nylon 6;

25 "Branched block ethylene polymer II" is a branched block ethylene polymer prepared from (i) 80 weight percent Tafmer\_ P-0180, a linear, narrow MWD ethylene polymer from Mitsui Petrochemical which contains polypropylene, and which has a density of 0.869 g/cm<sup>3</sup>, an I2 melt index of 4, and a maleic anhydride branch point; and (ii) 20 weight percent nylon 6; and

30 "Percent Ethylene Polymer" is the weight percent of ethylene polymer present in the blended composition, whether the ethylene polymer does not contain a branch point, is in the form of an E/MAH copolymer, or has been formed into a branched block ethylene polymer.



D 790. Results are reported in kpsi.

The following tests of physical and mechanical properties are performed on samples of the compositions of Examples 8-13 and Controls A-D, and the results of these tests are shown in Table II:

5

Rheology Index involves the viscosity of a sample determined from Rheometric Mechanical Spectroscopy, in which the sample is placed between plates which rotate reciprocatingly in the plane of the sample. The sample is heated to a specified temperature above its softening point, and viscosity is determined by the power required to force the plates to rotate at varying frequencies. Shown in Table II is a unitless value obtained as a ratio of the viscosity of the sample at 190°C when the plates are rotating at 0.1 radians/second divided by the viscosity at 100 radians/second.

15

Impact resistance ("Izod") is measured by the Izod test according to ASTM Designation D 256-84 (Method A) at 25°C. The notch is 10 mils (0.254 mm) in radius. Izod results are reported in ft-lb/in.

20

Impact resistance ("Weldline") is also measured by the Izod test according to ASTM Designation D 256-84 (Method A) at 25°C, but with respect to a sample which is formed with a butt weld in a double gated mold. The sample is unnotched, and it is placed in the vise so that the weld is 1 mm above the top surface of the vise jaws. Weldline

25

results are also reported in ft-lb/in, except as to Example 5 where "N.B." indicates that the sample did not break.

The dart drop impact test ("Dart Drop") is performed at 23°C by dropping a 100 pound weight which carries a ½" dart onto a circular test sample which is 1/8" thick. The weighted dart falls freely on a slotted track at 8050 in/min and impacts the sample, which is secured in position in the path of descent on an aluminum cast base. The value recorded in Table II is the energy required for the dart to break the sample, expressed in in-lb.

30

Deflection temperature under load ("D.T.U.L.") is measured in accordance with ASTM Designation D 648-82 at 66 psi. Results are reported in °F.

Flexural modulus ("F. Modulus") is determined according to ASTM

The data in Table III demonstrate that a branched block ethylene polymer is effective, when combined with a molding polymer such as a polyolefin resin, in producing a composition with a desirable balance of properties. A higher Rheology Index value is particularly notable because a higher value indicates greater shear sensitivity. A large numerator in this ratio shows that a material holds its melt strength at low shear, and a small denominator shows that a material undergoes shear thinning for easier processing, both of which typically are desirable qualities. The balance of properties shown for the examples is attained despite the fact that each of them contains less ethylene polymer than either Controls A or B. From the data in Table III, it can be concluded that a very effective means of utilizing an ethylene polymer in a blend composition is to use it to prepare a branched block ethylene polymer (as described herein), and then employ the branched block ethylene polymer as a modifier with a molding polymer. Compared to Controls A and B, the examples had greater surface durability and resistance to scratching.

The compositions of Examples 14-18 and Control E are prepared in the same manner as the compositions of Examples 8-13 and Controls A-D. The formulation content of Examples 14-18 and of Control E is given below in Table IV, in parts by weight of the total composition. In Table IV, "Polypropylene", "E/MAH Copolymer" and "Branched Block Ethylene Polymer I" are the same as in Table II. Branched block ethylene polymers prepared from smaller amounts of polyamide than branched block ethylene polymer I are used in the compositions of Examples 14-17, however, and these are designated in Table IV as follows:

"Branched Block Ethylene Polymer III" is a branched block ethylene polymer prepared from 90 weight percent "substantially linear" ethylene polymer, having an I2 melt index of about 0.5 and containing a maleic anhydride branch point; and 10 weight percent nylon 6;

"Branched Block Ethylene Polymer IV" is a branched block ethylene polymer prepared from 85 weight percent "substantially linear" ethylene polymer, having an I2 melt index of about 0.5

Table III  
Properties of  
Examples 8-13 and Controls A-D

	Controls				Examples							
	A	B	C	D	8	9	10	11	12	13		
Rheology Index	4.9	4.7	5.9		10.4	18.2	25.4		16.5			
Izod, ft-lb/in	0.4	2.0	2.8	1.6	2.4	12.1	15.2	3.2	5.7	10.6		
Weldline, ft-lb/in	7.6	8.0	4.5	2.5	17.3	16.8	22.4	11.8	4	N.B.		
Dart Drop, in-lb	65	304	282	230	344	341	314	312	279	237		
D.T.U.L., °F	170	140	138	149	142	140	134					
F. Modulus, kpsi	159	112	120	155	114	113	104					

Table IV  
Content of Examples 14-18 and Control E

	Control	Examples					
		14	15	16	17	18	
	E						
Polypropylene	1,500	1,500	1,500	1,500	1,500	1,500	
E/MAH Copolymer	500						
Branched Block Ethylene Polymer I						500	
Branched Block Ethylene Polymer III		500					
Branched Block Ethylene Polymer IV			500				
Branched Block Ethylene Polymer V				500			
Branched Block Ethylene Polymer VI					500		
Percent nylon in the Branched Block Ethylene Polymer	0	10	15	20	25	30	
Percent nylon, composition	0	2.5	3.75	5.0	6.25	7.5	

and containing a maleic anhydride branch point; and 15 weight percent nylon 6;

5 "Branched Block Ethylene Polymer V" is a branched block ethylene polymer prepared from 80 weight percent "substantially linear" ethylene polymer, having an I2 melt index of about 0.5 and containing a maleic anhydride branch point; and 20 weight percent nylon 6; and

10 "Branched Block Ethylene Polymer VI" is a branched block ethylene polymer prepared from 75 weight percent "substantially linear" ethylene polymer, having an I2 melt index of about 0.5 and containing a maleic anhydride branch point; and 25 weight percent nylon 6.

15 Percent nylon by weight is also set forth in Table III for each of the branched block ethylene polymer and for each composition as a whole.

20 The same tests for physical and mechanical properties are performed on Examples 14-18 and Control E as are performed on Examples 7-13 and Controls A-D, except that melt strength for each branched block ethylene polymer is determined using a pulley/drum type melt tension tester, as described above, and is measured in centiNewtons.

25 The results of such tests are set forth in Table V.

Table V  
Properties of  
Examples 14-18 and Control E

	Control	Examples						
		14	15	16	17	18		
Izod, ft-lb/in	E							
	2.8	2.5	3.2	8.3	9.7	12.1		
Weldline, ft-lb/in	4.5	5.4	6.8	9.4	9.9	16.8		
Dart Drop, in-lb	282	310	310	306	305	341		
Rheology Index	5.9	11.5	11.4	12.7	14.1	18.2		
D.T.U.L., °F	138	144	138	141	144	140		
F. Modulus, kpsi	120	105	127	122	124	113		
Branched block ethylene polymer melt strength, cN	13.8	22.9	25.9	32.2	45.4	52.2		

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**NOT FURNISHED UPON FILING**



Table VI, Content and Properties  
of Examples 19-20 and Controls F-G

	Control F	Example 19	Control G	Example 20
Polypropylene	1,500	1,500	1,500	1,500
E/MAH Copolymer	350		350	
Nylon 6	150		150	
Branched Block Ethylene Polymer VI		500		500
Percent nylon, composition	7.5	7.5	7.5	7.5
Izod, ft-lb/in	1.6	12.1	2.0	12.7
Weldline, ft-lb/in	10.9	16.8	5.7	13.3
Dart drop, in-lb	320	341	288	314
D.T.U.L., °F	143	140	139	143
F. Modulus, kpsi	112	113	115	117
Method of mixing	extrusion	extrusion	Banbury	Banbury

The results of Examples 14-18 and Control E are further evidence of the balance of desirable properties obtainable from the used of a branched block ethylene polymer as a modifier in a blended composition. It can be seen that, within the ranges in which polyamide is used in this invention to form the final block of the branched block ethylene polymer, increasing the amount of polyamide used increases the Izod properties.

The compositions of Example 19 and Control F are prepared in the same manner as the compositions of Examples 8-18 and Controls A-E. The compositions of Example 20 and Control G (although containing materials from which a branched block ethylene polymer could have been, but was not, made) are prepared by mixing the components simultaneously in a Banbury mixer at 220°C for 12 minutes. The formulation content of Examples 19-20 and of Controls F-G is given below in Table V, in parts by weight of the total composition. In Table V, "Polypropylene", "E/MAH Copolymer" and "Branched block ethylene polymer VI" are the same as in Table III. "Nylon 6" is the same as in Table II. Percent nylon by weight is also set forth in Table VI for each composition as a whole.

Some of the same tests for physical and mechanical properties are performed on Examples 19-20 and Controls F-G as are performed on Examples 8-18 and Controls A-E, and results of such tests are also set forth in Table VI.

notably higher viscosity at a low shear rate than either an ethylene polymer or a branched ethylene polymer, and yet also shows a notably higher shear sensitivity than either of its precursors since its viscosity at high shear drops to about the same level as that displayed by an ethylene polymer or a branched ethylene polymer. The tan delta value of a branched block ethylene polymer is also superior to that of either an ethylene polymer or and a branched ethylene polymer, and is indicative of significantly high melt elasticity (high storage modulus) at low as well as at high shear.

10

Moreover, it is found that a branched block ethylene polymer has the corresponding effect on a blend of a molding polymer therewith. Such a blended composition displays greater melt strength and elasticity at low shear than a composition modified with just an ethylene polymer or a branched ethylene polymer, and yet such a blend is shear sensitive enough that it thins at high shear to essentially the same viscosity as does a branched ethylene polymer. For example, Figure 20 shows viscosity at various shear rates for polypropylene blended with an ethylene/branch point copolymer, and with a branched block ethylene polymer prepared from various levels of polyamide as the amine-functionalized copolymer. The blends containing a branched block ethylene polymer have a higher viscosity at low shear but thin at high shear to the same extent as the blend containing only an ethylene/branch point copolymer. Figure 21 shows, for the same group of blends, tan delta, which is lost modulus divided by storage modulus. The compositions in which polypropylene is blended with a branched block ethylene polymer, instead of just an ethylene/branch point copolymer, have a lower tan delta and thus a higher storage modulus. Higher storage modulus represents a greater amount of recoverable elasticity. The determination of tan delta values is based on known methods, such as those derived from Melt Rheology and Its Role in Plastics Processing, Dealy and Wissbrun, Van Nostrand, 1990.

35

These improvements in properties are believed to be related to a tendency of the branched block ethylene polymer to be dispersed in a blended composition in such manner that the amine-functionalized polymer is dispersed as sub-micron particles, having great uniformity of size, within particles of the branched ethylene polymer. By contrast, when an amine-functionalized polymer is simply mixed as a

40

The results of Examples 19-20 and Controls F-G demonstrate the importance, when blending branched ethylene polymer and an amine-functionalized polymer (such as a polyamide) with a molding polymer (such as a polyolefin resin), of performing the mixing under conditions such that a branched block ethylene polymer is formed from the branched ethylene polymer and the amine-functionalized polymer. Such conditions include either first preparing the branched block ethylene polymer in a separate apparatus and then blending it with the molding polymer, or mixing all three materials in the same apparatus, such as an extruder, but in a sequence which allows the amine-functionalized polymer to react with the branched ethylene polymer, to form the branched block ethylene polymer, before the presence of the molding polymer would hinder that reaction.

For instance, the composition of Control F is a blend with polypropylene of the components from which a branched block ethylene polymer could have been made. However, the preparation of Control F did not produce a branched block ethylene polymer in a blend with polypropylene because all three components of Control F are dry blended together and then melt mixed simultaneously in an extruder. When the same components are used in Example 19 to first prepare a branched block ethylene polymer, from an E/MAH branched ethylene polymer and a polyamide, the resulting blend with polypropylene produces a composition which shows notably higher Izod, Weldline and Dart drop values. Even when the simultaneous blending of the E/MAH branched ethylene opolymer, polyamide and a polyolefin resin occurs under the high temperature, high shear conditions of a Banbury mixer, as in Control G, the resulting properties of the blended composition are no better than those of Control F, and are notably inferior to those of Example 20, in which preparation of a branched block ethylene polymer is completed before melt mixing with a molding polymer is undertaken.

35

It is found, in general, that a branched block ethylene polymer exhibits improved rheological properties as compared to the components from which it is made. For example, a branched block ethylene polymer, when tested by dynamic mechanical spectroscopy, shows a

of forming a branched block ethylene polymer can be lost if an excessive amount of amine-functionalized polymer is used. The value added by the amine-functionalized polymer, which forms the final block on the branched block ethylene polymer, will be offset by free amine-functionalized polymer, which may crosslink or may form crystalline domains which are brittle and subject the blended composition to increased notch sensitivity.

The compositions of Examples 21-24 and Controls H and I are prepared using similar mixing conditions as the compositions of Examples 8-18 and Controls A-E. However, Controls H and I are representative of a situation in which a branched block ethylene polymer could have been prepared, but was not, since all components were mixed together rather than in a sequence which would allow formation of a branched block ethylene polymer. The formulation content of Examples 21-24 and Controls H and I is given below in Table VII, in parts by weight of the total composition. In Table VII:

"Polycarbonate" is 10 melt flow Bisphenol-A polycarbonate;

"Branched Block Ethylene Polymer VII" is a branched block ethylene polymer prepared from 70 weight percent E/MAH copolymer having an I2 melt index of 0.37; and 30 weight percent nylon 6;

"Epoxy" is a Bisphenol-A/epichlorohydrin epoxy resin, such as D.E.R.\_ 332 epoxy resin from The Dow Chemical Company;

E.S.O. is epoxidized soybean oil tackifier; and

IR 1076 is Irganox\_ 1076 stabilizer.

Also in Table VI, "Nylon 6", "Branched Block Ethylene Polymer I" and "E/MAH Copolymer" are the same as in Table II. Percent E/MAH Copolymer by weight is also set forth in Table VII for Controls H and I and Examples 16-17 as a whole.

Some of the same tests for physical and mechanical properties are performed on Examples 14-17 and Controls H and I as are performed on Examples 1-11 and Controls A-E. Other tests performed are as

component in a random, physical blend with an branched ethylene polymer without first being formed into a branched block ethylene polymer, the amine-functionalized polymer which is dispersed within the ethylene polymer has little or no uniformity of particle size; and  
5 the amine-functionalized polymer may also in such case be dispersed as large, multi-micron particles in the molding polymer matrix resin with no association to the ethylene polymer whatever.

Consequently, in a preferred embodiment, the amine-  
10 functionalized polymer in a branched block ethylene polymer is dispersed in an branched ethylene polymer as particles about 50% or more, often about 65% or more, frequently about 80% or more and occasionally about 90% or more of which have a size which is within about 80% to about 120% of the average size of the whole population of  
15 amine-functionalized polymer particles dispersed in the particle of branched ethylene polymer.

When an amine-functionalized polymer in a branched block ethylene polymer is dispersed in the branched ethylene polymer as a  
20 population of particles which are very uniformly of small size, the particles of branched ethylene polymer are themselves smaller and are more evenly distributed within the molding polymer matrix, which results in a composition which has superior elastomeric impact strength. By contrast, when an amine-functionalized polymer particle  
25 is merely a component in a random, physical blend with no branched block ethylene polymer terpolymer, branched ethylene polymer particles are larger and/or groups of branched ethylene polymer particles tend to agglomerate and create domains which effectively behave as if they were larger particles. Therefore, in another preferred embodiment,  
30 the ratio of the size of an branched ethylene polymer particle to the average size of an amine-functionalized polymer particle dispersed therein, when a branched block ethylene polymer has been prepared therefrom, is much lower than the ratio of the size of an branched ethylene polymer particle to the average size of an amine-  
35 functionalized polymer particle dispersed therein when a branched block ethylene polymer has not been formed and the amine-functionalized polymer is merely a component in a random, physical blend.

40 Correspondingly, the beneficial effect in a blended composition

Table VII, Content of Examples 21-24 and Controls H-I

	Example 21	Example 22	Control H	Example 23	Control I	Example 24
Polycarbonate	1850	1850				
Nylon 6			1700	1570	1600	1428
Branched Block Ethylene Polymer I				430		572
Branched Block Ethylene Polymer VII	150	150				
E/MAH Copolymer			300		400	
Epoxy		4				
E.S.O.	2	2				
IR 1076	4	4				
Percent E/MAH Copolymer in composition			15	15	20	20

follows:

Tensile strength at break and percent elongation at break are both measured in accordance with ASTM Designation D 638-84.

5

Gloss measurements are performed on testing samples according to ASTM Designation D 523-85 using a Dr. Lange Reflectometer RB3 available from Hunter Associates.

10 The results of each of these tests are set forth in Table VII. N.B. indicates no break in the weldline test.



The results of Controls H and I and Examples 23 and 24 demonstrate that an Ethylene/MAH Copolymer, when used by itself as an impact modifier without having been formed into a branched block ethylene polymer, does not enhance impact properties to the same extent that a branched block ethylene polymer does. An Ethylene/MAH Copolymer has a lower viscosity and a lower elasticity than a branched block ethylene polymer. Consequently, when an amine-functionalized polymer is utilized as just another blend component rather than being utilized to prepare a branched block ethylene polymer, the resulting composition is not characterized by impact properties, particularly at low temperature, which are as desirable as a composition of a block.

Examples using branched block ethylene polymers in which the reactive thermoplastic polymer of subcomponent (c) is a polyester.

The composition of Example 25 is a blend with polycarbonate of a branched block ethylene polymer. The composition of Control A1 is a blend with polycarbonate of the three components from which a branched block ethylene polymer could have been made. However, the preparation of Control A did not result in a blend with polycarbonate of a branched block ethylene polymer because all four materials were blended simultaneously. The composition of Control B1 is a blend with polycarbonate of an ethylene polymer containing only a maleic anhydride branch point ("E/MAH copolymer"). The composition of Controls C1 and D1 is each a blend with polycarbonate of a substantially linear ethylene polymer which does not contain a branch point. The compositions of Controls E1, F1, and G1 is each a blend with polycarbonate of another type of olefin polymer.

The branched block ethylene polymer contained in the composition of Example 25 is prepared by melt blending in a 30 mm Werner & Pfleiderer extruder a mixture of 30 weight percent poly(butylene terephthalate) and 70 weight percent "substantially linear" ethylene polymer containing a maleic anhydride branch point ("E/MAH Copolymer"). The maleic anhydride branch point is formed on the "substantially linear" ethylene polymer in an amount of 1 weight

Table VIII, Properties of Examples 21-24 and Controls H-I

	Example 21	Example 22	Control H	Example 23	Control I	Example 24
Izod, ft-lb in, 23°C	13.7	13.7	6.7	8.2	5.6	7.5
Izod, ft-lb in, 0°C	12.8	13.1	6.6	9.0	6.9	8.9
Izod, ft-lb in, -20°C	11.7	10.6	2.4	2.8	3.6	9.0
Izod, ft-lb in, -30°C						9.6
Weldline, ft-lb/in	3.0	7.0	N.B.	N.B.	N.B.	N.B.
20° Gloss	18	19				
60° Gloss	69	70				
Tensile Strength	8030	8791	5828	5602	7001	6619
Percent Elongation	84	111	41	60	181	189
D.T.U.L., °F	291	288	289	335	299	307
F. Modulus, kpsi	290	299	205	198		228

"POE" is a "substantially linear" ethylene polymer which does not contain a maleic anhydride branch point, having a 0.5 I2 melt index;

"ECO" is ethylene/carbon monoxide copolymer;

5

"HDPE" is high density polyethylene having a density of about 0.96 g/cm<sup>3</sup> and an I2 melt index (according to ASTM D 1238) of about 10; and

10 "LLDPE" is a linear low density polyethylene having an I2 melt index (according to ASTM D 1238) of about 4.

The following tests are performed on Example 25 and Controls A1-G1, and the results of these test are also shown in Table I:

- 15 Impact resistance is measured by the Izod test ("Izod") according to ASTM Designation D 256-84 (Method A) at 25°C. The notch is 10 mils (0.254 mm) in radius. Impact is parallel to the flow lines in the plaque from which the bar is cut in one sample of each composition and is perpendicular to flow lines in another sample. The ratio of the
- 20 Izod result in the case of impact parallel to flow lines to that of impact perpendicular to flow lines is set forth as a unitless value labeled "Anisotropy". The Izod results are then used to estimate the ductile/brittle transition temperature ("DBTT") of each sample.
- 25 Impact resistance is also measured by the Izod test ("Weldline") according to ASTM Designation D 256-84 (Method A) at 25°C, but with respect to a sample which is formed with a butt weld in a double gated mold. The sample is unnotched, and it is placed in the vise so that the weld is 1 mm above the top surface of the vise jaws. Weldline results are reported in kg-cm/cm.

30

percent, based on the weight of the E/MAH Copolymer, using a peroxide initiator. The conditions used in preparation of the branched block ethylene polymer are: zone temperatures of 150, 200, 250, 250 and 250°C; 250 rpm; 70-85 percent torque; and a 30 second residence  
5 time.

The final compositions of Example 25 and Controls A1-G1 are prepared by mixing the dry components of each on a paint shaker for 5 minutes, and then feeding the dry-blended formulation to the Werner &  
10 Pfleiderer extruder under the same conditions used to prepare the branched block ethylene polymer, except that the zone temperatures are 150, 200, 280, 280 and 280°C. The extrudate is cooled in the form of strands and is then comminuted as pellets. The pellets are dried in  
15 an air draft oven for 3 hours at 120°C, and are then used to prepare test specimens on a 70 ton Arburg molding machine on which the barrel temperature is 280°C, the mold temperature is 82°C, and the screw speed is 120 rpm.

The formulation content of Example 25 and of Controls A1-G1 is  
20 given below in Table I, in parts by weight of the total composition. In Table I:

"Polycarbonate" is a Bisphenol-A polycarbonate having a weight  
25 average molecular weight of approximately 28,000;

"Branched block ethylene polymer" is a branched block ethylene polymer prepared from poly(butylene terephthalate) and a "substantially  
linear" ethylene polymer containing a maleic anhydride branch point,  
as described above;

30 "E/MAH Copolymer" is a substantially linear ethylene polymer containing a maleic anhydride branch and having a 0.5 I2 melt index;

"PBT" is poly(butylene terephthalate);  
35

The data in Table IX demonstrate that a branched block ethylene polymer is effective, when combined with a molding polymer, in producing a composition with a desirable balance of properties.

- 5 Control A1, which contains the components from which a branched block ethylene polymer in a PC blend could have been made but was not, has a weldline value much lower than that of Example 25. The other controls, which each contain some other form of olefin polymer, have properties which are, in individual categories, quite good, but none  
10 of them has as desirable a balance in all three categories as Example 25. For instance, Controls C1-E1 all have an impressive level of anisotropy but suffer from very low weldline. From the data in Table VIII, it can be concluded that a very effective means of utilizing an olefin polymer in a blend composition is to use it to prepare a  
15 branched block ethylene polymer (as described herein), and then employ the branched block ethylene polymer as a blending modifier with a molding polymer.

- These improvements in properties are believed to be related to a tendency of the branched block ethylene polymer to be dispersed in a  
20 blended composition in such manner that the polyester is dispersed as sub-micron particles, having great uniformity of size, within particles of the ethylene/branch point copolymer. By contrast, when a polyester is simply mixed as a component in a random, physical blend with an ethylene/branch point copolymer without first being formed  
25 into a branched block ethylene polymer, the polyester which is dispersed within the ethylene polymer has little or no uniformity of particle size; and the polyester may also in such case be dispersed as large, multi-micron particles in the molding polymer matrix resin with no association to the ethylene polymer whatever.

30

Table IX, Content and Properties  
of Controls A1-G1 and Example 25

of Controls A1-G1 and Example 25											
	Controls										Example 25
	A1	B1	C1	D1	E1	F1	G1				
Polycarbonate	93	95	93	95	95	95	95				93
Branched block ethylene polymer											7
E/MAH Copolymer	4.9	5									
PBT	2.1		2.1								
POE			4.9	5							
ECO					5						
HDPE						5					
LLDPE							5				
Anisotropy	.678	.748	.853	.879	.838	.575	.672				.783
DBTT, °C	-35	-45	-20	-20	-20	-40	-30				-35
Weldline, kg-cm/cm	32	26	17	5	7	29	12				83

in a random, physical blend with no terpolymer formation, ethylene/branch point copolymer particles are larger and/or groups of ethylene/branch point copolymer particles tend to agglomerate and create domains which effectively behave as if they were larger particles. Therefore, in another preferred embodiment, the ratio of the size of an ethylene/branch point copolymer particle to the average size of a polyester particle dispersed therein, when a branched block ethylene polymer has been prepared therefrom, is much lower than the ratio of the size of an ethylene/branch point copolymer particle to the average size of a polyester particle dispersed therein when a block copolymer has not been formed and the polyester is merely a component in a random, physical blend.

The compositions of Examples 26-29 are prepared in a similar manner as the composition of Example 25. The branched block ethylene polymer used in the compositions of Examples 26-28 was prepared by reacting poly(ethylene terephthalate), having an intrinsic viscosity of 0.59, and a "substantially linear" ethylene polymer containing a maleic anhydride branch point in the presence of potassium paratolyl sulfimide ("KPTSM") catalyst. Although the branched block ethylene polymer prepared with the benefit of catalyst is more preferred, that which is prepared without catalyst, such as used in Example 26, is still a useful product. The branched block ethylene polymer used in each example is prepared from 30 weight percent "substantially linear" ethylene polymer containing a maleic anhydride branch point and 70 weight percent poly(ethylene terephthalate). Each blended composition is prepared from 93 weight percent polycarbonate and 7 weight percent branched block ethylene polymer. The amount of KPTSM catalyst used in Examples 27-29, expressed in weight parts per million measured with respect to the combined weight of the E/MAH Copolymer and the poly(ethylene terephthalate) from which the branched block ethylene polymer is made, is shown in the following table.

The impact resistance of Examples 26-29 is measured by the Izod test according to ASTM Designation D 256-84 (Method A) at 25°C with respect to a "weldline" sample which is formed with a butt weld in a double gated mold. The sample is unnotched, and it is placed in the vise so that the weld is 1 mm above the top surface of the vise jaws. Izod results for Examples 26-29 are reported for 11 trials of the composition of each example, and the results of each of those 11

Consequently, in a preferred embodiment, the polyester in a branched block ethylene polymer is dispersed in an ethylene/branch point copolymer as particles about 50% or more, often about 65% or more, frequently about 80% or more and occasionally about 90% or more  
5 of which have a size which is within about 80% to about 120% of the average size of the whole population of polyester particles dispersed in the particle of ethylene/branch point copolymer.

When a polyester in a branched block ethylene polymer is dispersed in the ethylene/branch point copolymer as a population of  
10 particles which are very uniformly of small size, the particles of ethylene/branch point copolymer are themselves smaller and are more evenly distributed within the molding polymer matrix, which results in a composition which has superior elastomeric impact strength. By contrast, when a polyester particle is merely a component



	Examples			
	26	27	28	29
Amount of KPTSM, ppm	0	500	1,000	2,000
Samples out of 11 with no break	3	7	7	7
Samples out of 11 with partial break	5	2	4	4
Samples out of 11 with brittle break	3	2	0	0
Unnotched Izod, ft-lb/in	20	20	34	43
Standard deviation - Izod, ft-lb/in	13	15	2	1

5 The results of Examples 26-29 demonstrate that the presence of KPTSM as a catalyst, during the preparation of the branched block ethylene polymer used as a blending modifier in the compositions of Examples 27-29, produced a branched block ethylene polymer which made a better contribution to the impact strength of the composition than did the branched block ethylene polymer prepared without benefit of a catalyst. While the composition of Example 26 showed a very respectable Izod value, the compositions of Examples 27-29 showed improved Izod and fewer brittle breaks as greater amounts of the KPTSM catalyst were used during preparation of the branched block ethylene polymer used in the blend.

15

Example 30: Use of Branched Block Ethylene Polymers Wherein the Reactive Thermoplastic Polymer is Polycaprylactone

20 Bisphenol A polycarbonate with a weight average molecular weight of 18,000 grams/mole was used as the base resin. The polyolefin phase used was a substantially linear ethylene/1-octene polymer having a density of 0.88 g/cc and an I2 of 30 g/10 min. The ethylene/propylene/non-conjugated diene elastomer grafted with styrene/acrylonitrile was obtained from Uniroyal Chemical under the tradename Royaltuff 372P20 (SAN-g-EPDM). The poly(caprolactone) (PCL) 25 was obtained from Union Carbide under the tradename Tone P-767.

5 trials are clasified as either "no break", "partial break" or "brittle break". A brittle break of a sample in the following table refers to a break which resulted in separation of the sample into two distinct pieces, whereas in a partial break, the sample is not cleanly separated and the major portions remain hinged. The numerical Izod value reported for each example is the average of that value for those of the 11 trials of each which were partial or brittle breaks. Izod results are reported in ft-lb/in, as is the standard deviation of the Izod values for each group of partial or brittle breaks.

## Performance attributes

5

	Molded PC (Mw) g/mol	Nu at 80 sec <sup>-1</sup>	Nu at 2900 sec <sup>-1</sup>	DBTT	Room temp. IZOD
Control 1	18500	191	108	greater than 30	2.2
Control 2	18500	152	70	-5	0
Example 1	18700	174	84	-20	8.8
Control 3	19200		100	-20	8.3
Example 2	18800	180	75	-10	9.1
Example 3	18600	163	72		8.8

A 70/30 weight ratio of MAH-g-EO was dry blended with PCL in a tumbler. The mixture was pelletized using a 30 mm Werner & Pfleiderer co-rotating twin-screw extruder. Extrusion conditions were screw speed set at 245 rpm and barrel temperatures set at 190, 260, 160, 260°C and die temperature set at 260°C. The following are the resin compositions:

## Resin Compositions

10

	Polycarbonate (80 MFR)	Homogeneous Ethylene Polymer (0.88 g/cc, 30 g/10 min.)	PCL-g-EO	SAN-g-EPDM
Control 1	100			
Control 2	90	10		
Example 1	90		10	
Control 3	90			10
Example 2	90	9	1	
Example 3	90	9		1

Molecular weight analysis: size exclusion chromatograph technique couples with a UV detector using methylene chloride as the solvent and tetrahydrofuran as the solvent carrier. Calibration was done with LEXAN polycarbonate standard.

15

Viscosity (Nu): shear viscosity was determined using a capillary rheometer and circular die with dimension of 1.27 mm inner diameter and 25.4 mm length. The temperature used was 270°C. The reported values were viscosity at 80 and 2900 sec<sup>-1</sup>.

20

Izod Impact: Izod impact values were determined on a 0.25 mm (10 mils) prenotched sample. Tests were run using a 10 ft-lb pendulum.

Ductile brittle transition temperature (DBTT): the temperature at which the sample has izod impact fracture going from ductile to brittle.

25

7. The branched block ethylene polymer of Claim 1 wherein the narrow polydispersity ethylene polymer is a substantially linear ethylene polymer which is characterized as having

- 5       (i) a melt flow ratio  $I_{10}/I_2$  which is greater than or equal to 5.63, a
- (ii) a molecular weight distribution defined by  $M_w/M_n$  which is less than or equal to  $(I_{10}/I_2)-4.63$ , and
- (iii) a critical shear rate at the onset of surface melt fracture at least about 50 percent greater than a linear ethylene
- 10       polymer having essentially the same  $I_2$  and  $M_w/M_n$ , each within 90-110 percent of the corresponding value for the substantially linear ethylene polymer; and
- (iv) a single melting point as determined by differential scanning calorimetry between about 30 ° C and 150° C
- 15       wherein the substantially linear ethylene polymer is further characterized as having a SCBD Index of greater than 50 percent.

8. The branched block ethylene polymer of Claim 7 wherein the substantially linear ethylene polymer has a critical shear stress at

20       the onset of gross melt fracture greater than about  $4 \times 10^6$  dyne/cm<sup>2</sup>.

9. The branched block ethylene polymer of Claim 7 wherein the substantially linear ethylene polymer has an average of about 0.01 to about 3 long chain branches/1000 total carbon atoms.

25       10. The branched block ethylene polymer of Claim 8 wherein the substantially linear ethylene polymer has a processing index less than or equal to about 70 percent of the processing index of a linear ethylene polymer as to which the  $I_2$ , polydispersity and density is

30       each within 90-110 percent of the corresponding value for the substantially linear ethylene polymer.

11. The branched block ethylene polymer of Claim 1, wherein the reactive thermoplastic polymer is an amine-functionalized polymer.

35

What is claimed is:

1. A branched block ethylene polymer comprising
  - (a) an ethylene polymer;
  - 5 (b) an ethylenically unsaturated functionalized organic compound; and
  - (c) a reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated functionalized organic compound.
- 10 2. The branched block ethylene polymer of Claim 1 wherein the ethylenically unsaturated functionalized organic compound contains a carbonyl group.
- 15 3. The branched block ethylene polymer of Claim 1 wherein the ethylenically unsaturated functionalized organic compound is maleic anhydride.
- 20 4. The branched block ethylene polymer of Claim 1 wherein the ethylenically unsaturated functionalized organic compound carries an epoxy ring.
- 25 5. The branched block ethylene polymer of Claim 1 wherein the ethylenically unsaturated functionalized organic compound is an oxazoline, amine or alcohol.
6. The branched block ethylene polymer of claim 1, wherein the ethylene polymer is a homogeneous ethylene polymer having:
  - (i) a Mw/Mn ratio, as determined by gel permeation
  - 30 chromatography, of less than about 3.0;
  - (ii) a density of about 0.93 g/cm<sup>3</sup> or less; and
  - (iii) a Short Chain Branching Distribution Index of greater than about thirty percent; and
  - (iv) a single melting peak as determined by differential
  - 35 scanning calorimetry between -30°C and 150°C.

17. The method of Claim 15 wherein the reactive thermoplastic polymer is reacted with the branched ethylene polymer in the presence of a catalyst selected from an alkali metal or alkaline earth metal salt having a pKa of 7 or more, and a nitrogen-containing organic base.

18. The method of Claim 15 wherein the catalyst is an amine.

10 19. The method of Claim 15 wherein the catalyst is derived from an aromatic sulfimide.

20. The method of Claim 15 wherein the catalyst is potassium paratolyl sulfimide.

15

21. The method of Claim 15 wherein both the formation of the ethylenically unsaturated organic compound branch off of the ethylene polymer, and (2) the reaction of the reactive thermoplastic polymer with the ethylene polymer are performed in a single pass through one extruder.

20

22. A blend of a thermoplastic blending or molding polymer with a branched block ethylene polymer which in turn comprises

- 25 (a) an ethylene polymer;  
(b) an ethylenically unsaturated functionalized organic compound;  
and  
(c) a reactive thermoplastic polymer capable of reacting with the ethylenically unsaturated functionalized organic compound.

30 23. The blend of Claim 22, wherein the ethylene polymer is a homogeneous ethylene polymer which has:

- (i) a Mw/Mn ratio, as determined by gel permeation chromatography, of less than about 3.0;  
(ii) a density of about 0.93 g/cm<sup>3</sup> or less;  
35 (iii) a Short Chain Branching Distribution Index of greater than about thirty percent; and

13. The branched block ethylene polymer of Claim 1, wherein the reactive thermoplastic polymer is a polyester.

14. A method of preparing a branched block ethylene polymer which  
5 contains

(a) an ethylene polymer;

(b) an ethylenically unsaturated functionalized organic compound;

and

(c) a reactive thermoplastic polymer capable of reacting with the  
10 ethylenically unsaturated functionalized organic compound;

said method comprising (1) forming the ethylenically unsaturated functionalized organic compound into a branch off of the ethylene polymer to form a branched ethylene polymer, and thereafter (2) reacting the reactive thermoplastic polymer with the branched ethylene  
15 polymer.

15. The method of Claim 14, wherein the ethylene polymer is a homogeneous ethylene polymer having:

(i) a Mw/Mn ratio, as determined by gel permeation  
20 chromatography, of less than about 3.0;

(ii) a density of about 0.93 g/cm<sup>3</sup> or less;

(iii) a Short Chain Branching Distribution Index of greater than about thirty percent; and

(iv) a single melting peak as determined by differential  
25 scanning calorimetry between -30°C and 150°C.

16. The method of Claim 15, wherein the ethylene polymer is a substantially linear ethylene polymer which is characterized as having

(i) a melt flow ratio  $I_{10}/I_2$  which is greater than or  
30 equal to 5.63, a

(ii) a molecular weight distribution defined by  $M_w/M_n$  which is less than or equal to  $(I_{10}/I_2)-4.63$ , and

(iii) a critical shear rate at the onset of surface melt fracture at least about 50 percent greater than a linear ethylene  
35 polymer having essentially the same  $I_2$  and  $M_w/M_n$ , and

(iv) a SCBD Index of greater than 50 percent.



functionalized organic compound; and a reactive thermoplastic polymer, comprising:

- 5 (1) forming a branched block ethylene polymer by
  - a) adding the ethylenically unsaturated functionalized organic compound to the ethylene polymer to form a branched ethylene polymer, and thereafter
  - b) reacting the reactive thermoplastic polymer with the residue of the ethylenically unsaturated functionalized organic compound; and thereafter
- 10 (2) blending the branched block ethylene polymer with the thermoplastic molding polymer.

32. The method of Claim 31 wherein the ethylene polymer is a homogenous ethylene polymer having:

- 15 (i) a polydispersity of less than about 3.0;
- (ii) a density of about 0.93 g/cm<sup>3</sup> or less;
- (iii) a Short Chain Branching Distribution Index of greater than about thirty percent; and
- (iii) a single melting peak as determined by differential
- 20 scanning calorimetry between -30°C and 150°C;

33. The method of Claim 31 wherein the reactive thermoplastic polymer is reacted with the branched narrow ethylene polymer in the presence of a catalyst selected from an alkali metal or alkaline earth metal salt having a pKa of 7 or more, and a nitrogen-containing organic base.

34. The method of Claim 31 wherein (a) the formation of the unsaturated functionalized organic compound into a branch off of the ethylene polymer, (b) the reaction of the reactive thermoplastic polymer with the branched ethylene polymer, and (c) the blending of the branched block ethylene polymer with the blending or molding thermoplastic resin are all performed in a single pass through one extruder.

35

(iv) a single melting peak as determined by differential scanning calorimetry between -30°C and 150°C.

24. The blend of Claim 22, wherein the ethylene polymer is a  
5 substantially linear ethylene polymer which is characterized as having

(i) a melt flow ratio  $I_{10}/I_2$  which is greater than or equal to 5.63, a

(ii) a molecular weight distribution defined by  $M_w/M_n$  which is less than or equal to  $(I_{10}/I_2)-4.63$ , and

10 (iii) a critical shear rate at the onset of surface melt fracture at least about 50 percent greater than a linear ethylene polymer having essentially the same  $I_2$  and  $M_w/M_n$ , and

(iv) a SCBD Index of greater than 50 percent.

25. The blend of Claim 22 wherein the thermoplastic blending or  
15 molding polymer is selected from the group consisting of polycarbonate, polyester, poly(phenylene ether), polysulfone, polyetherimide, polypropylene, and polyethylene.

26. The blend of Claim 22 wherein the thermoplastic blending or  
20 molding polymer is a substantially linear ethylene polymer.

27. The blend of Claim 22, further comprising a styrenic copolymer, an elastomeric impact modifier, a flow aid, or a mixture thereof.

25 28. The blend of Claim 22, further comprising at least one of an oil or a filler.

29. The blend of Claim 22, wherein the reactive thermoplastic polymer is nylon 6.

30

30. The blend of Claim 22 in the form of a molded or extruded article.

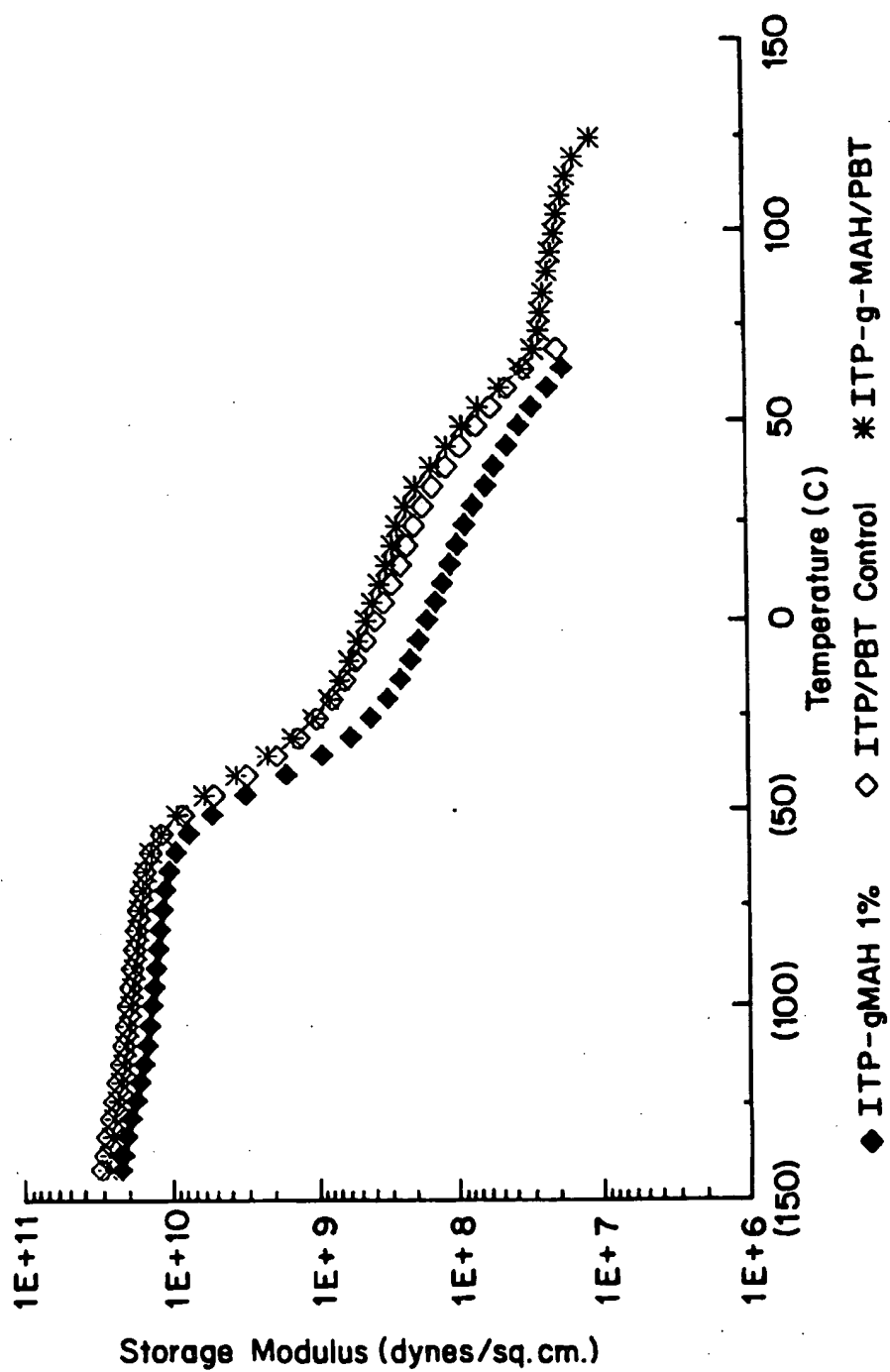
31. A method of preparing a composition from a thermoplastic  
35 molding polymer, an ethylene polymer; an ethylenically unsaturated



35. The method of Claim 31 wherein a branched ethylene polymer and the reactive thermoplastic polymer are fed together into an extruder, and the blending or molding resin is fed through a downstream port during the same pass through said extruder.

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FIG. 1



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FIG. 2A

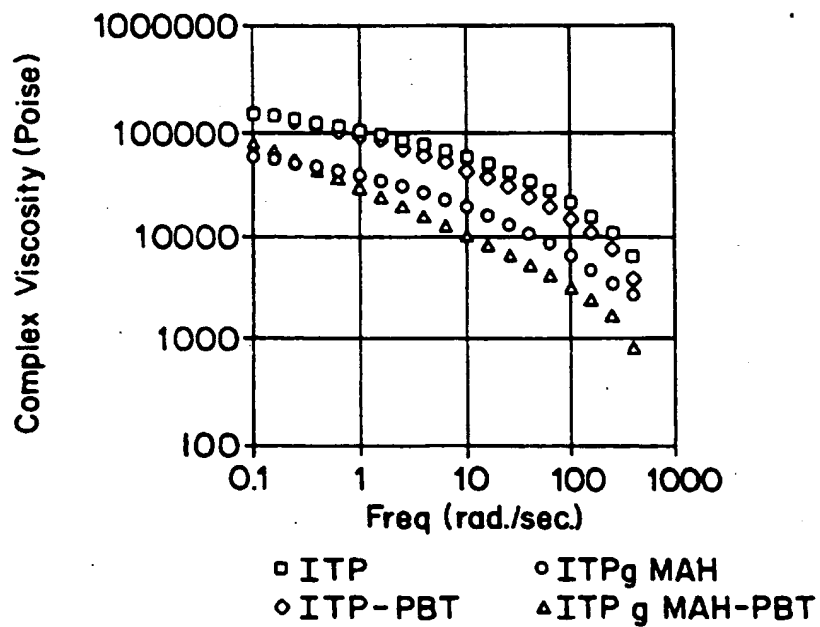
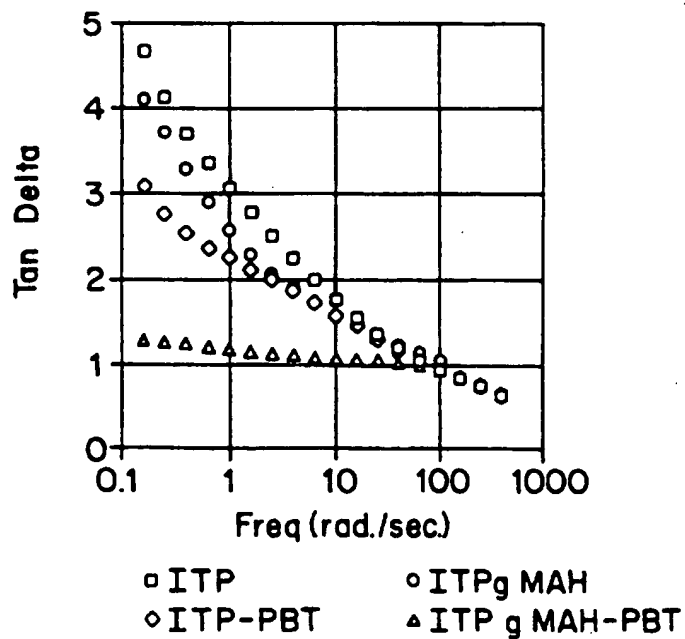
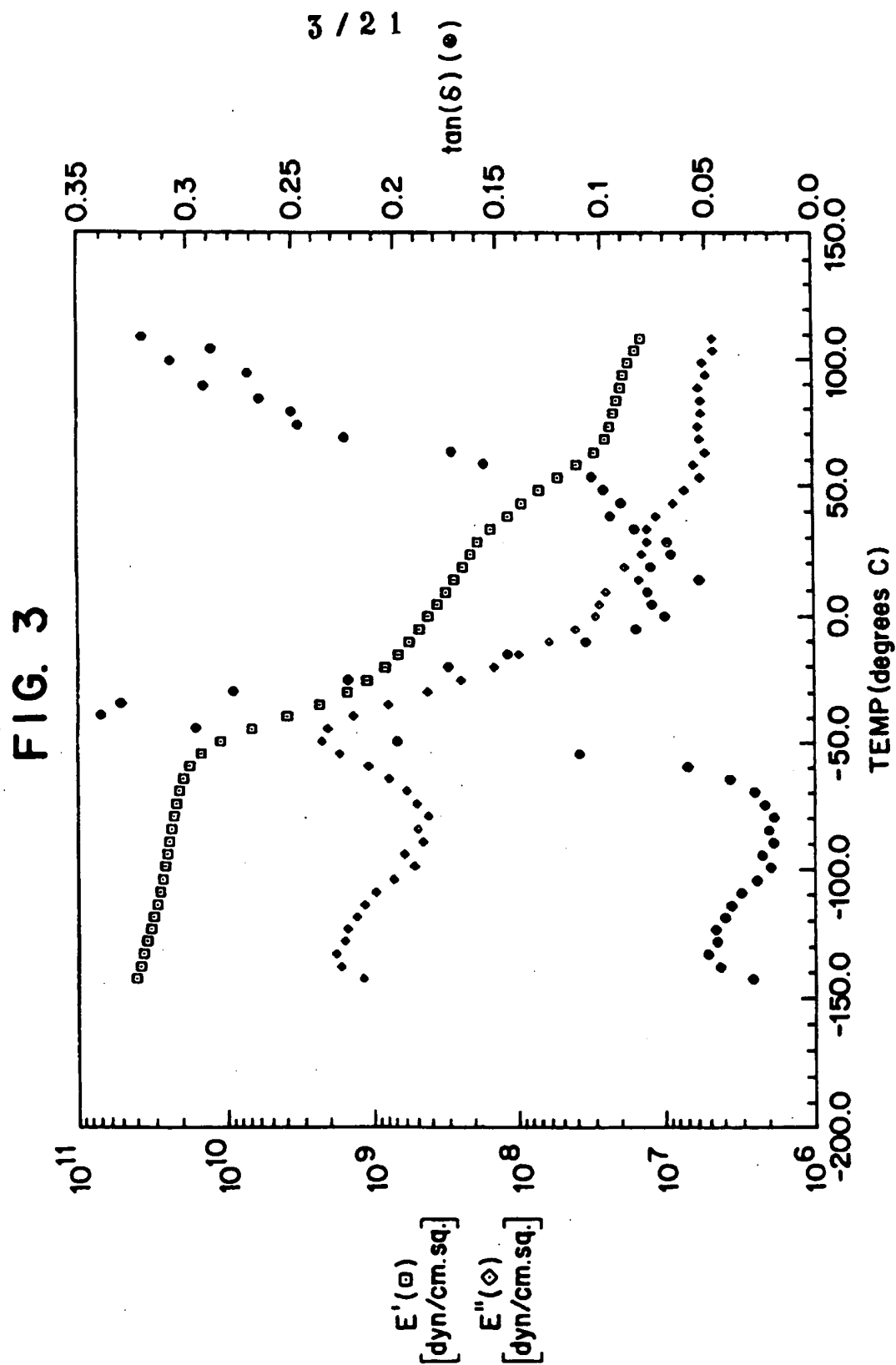


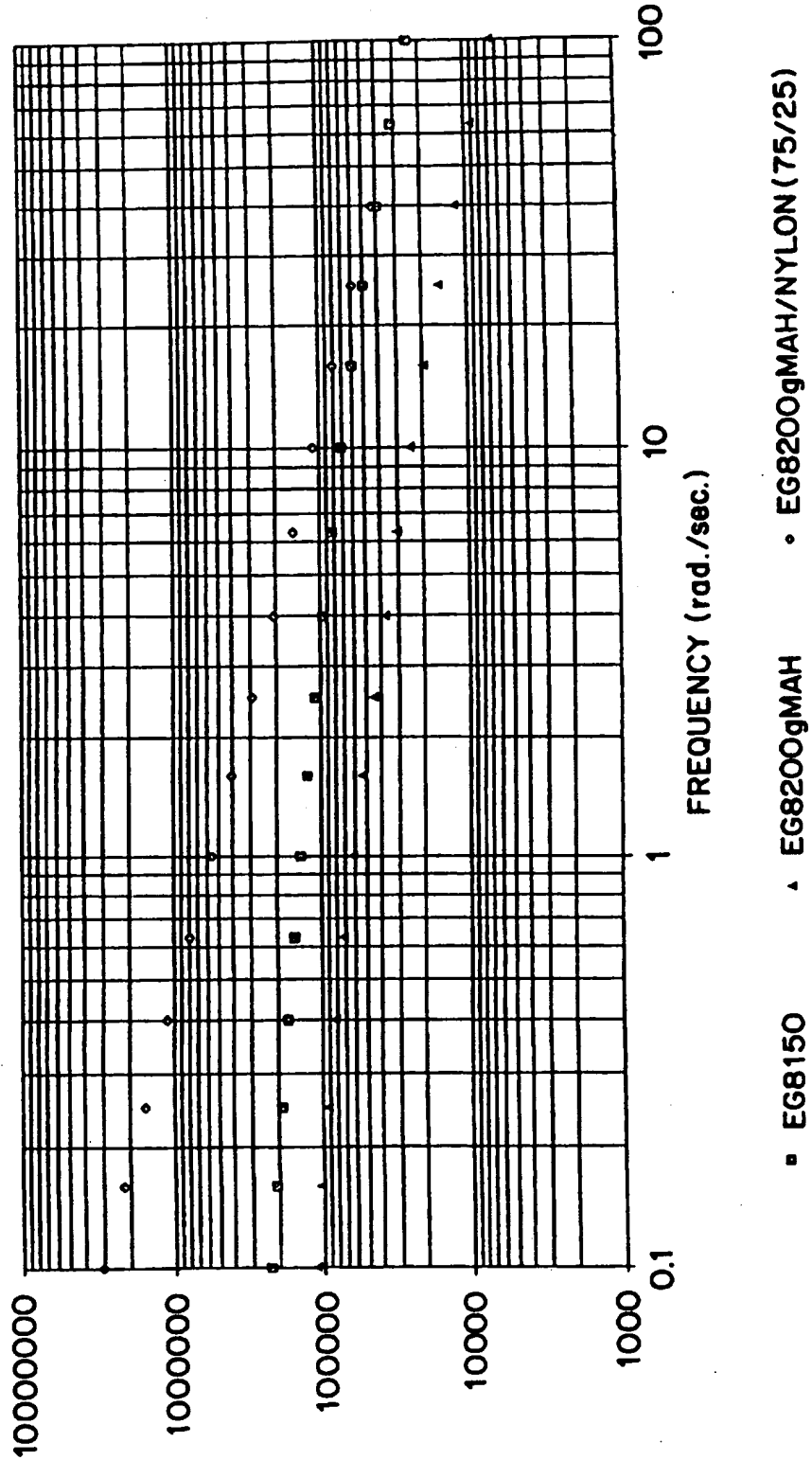
FIG. 2B





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FIG. 4

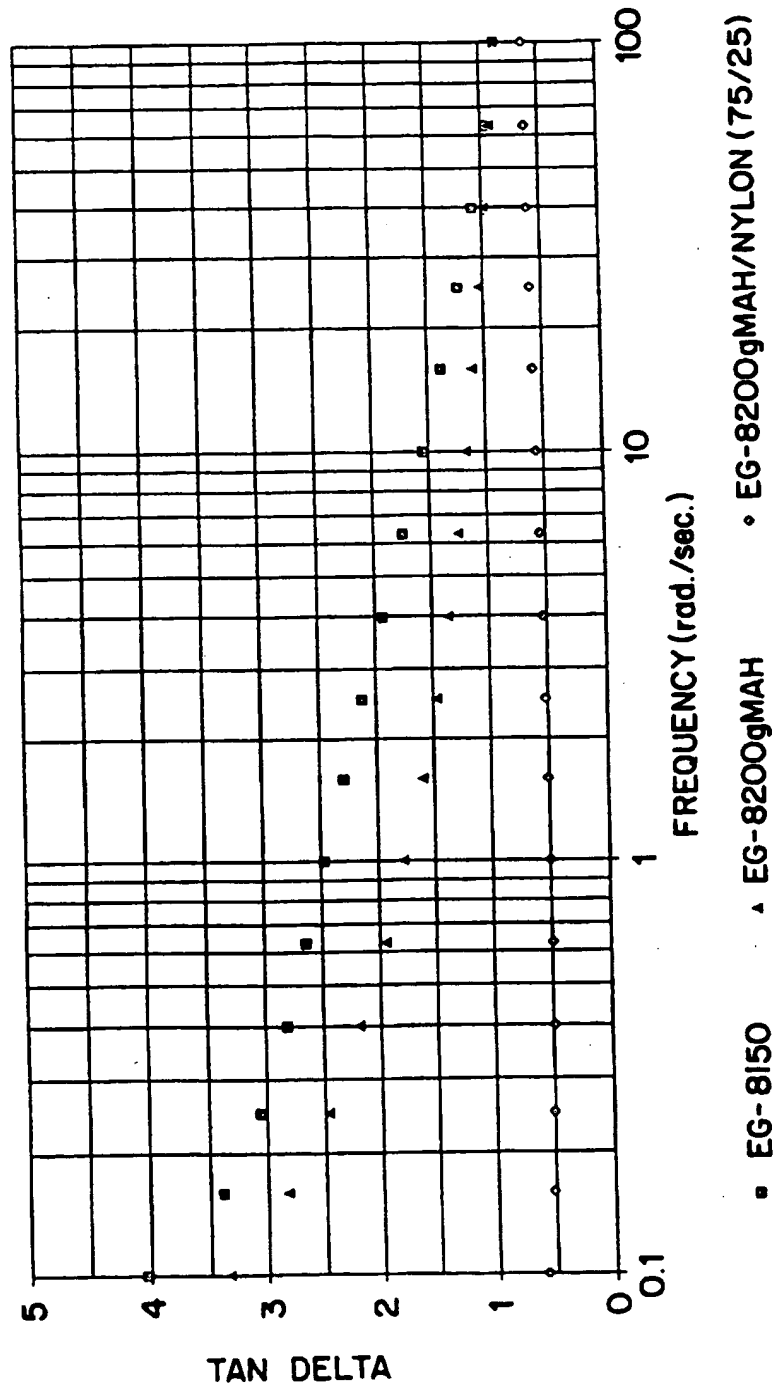


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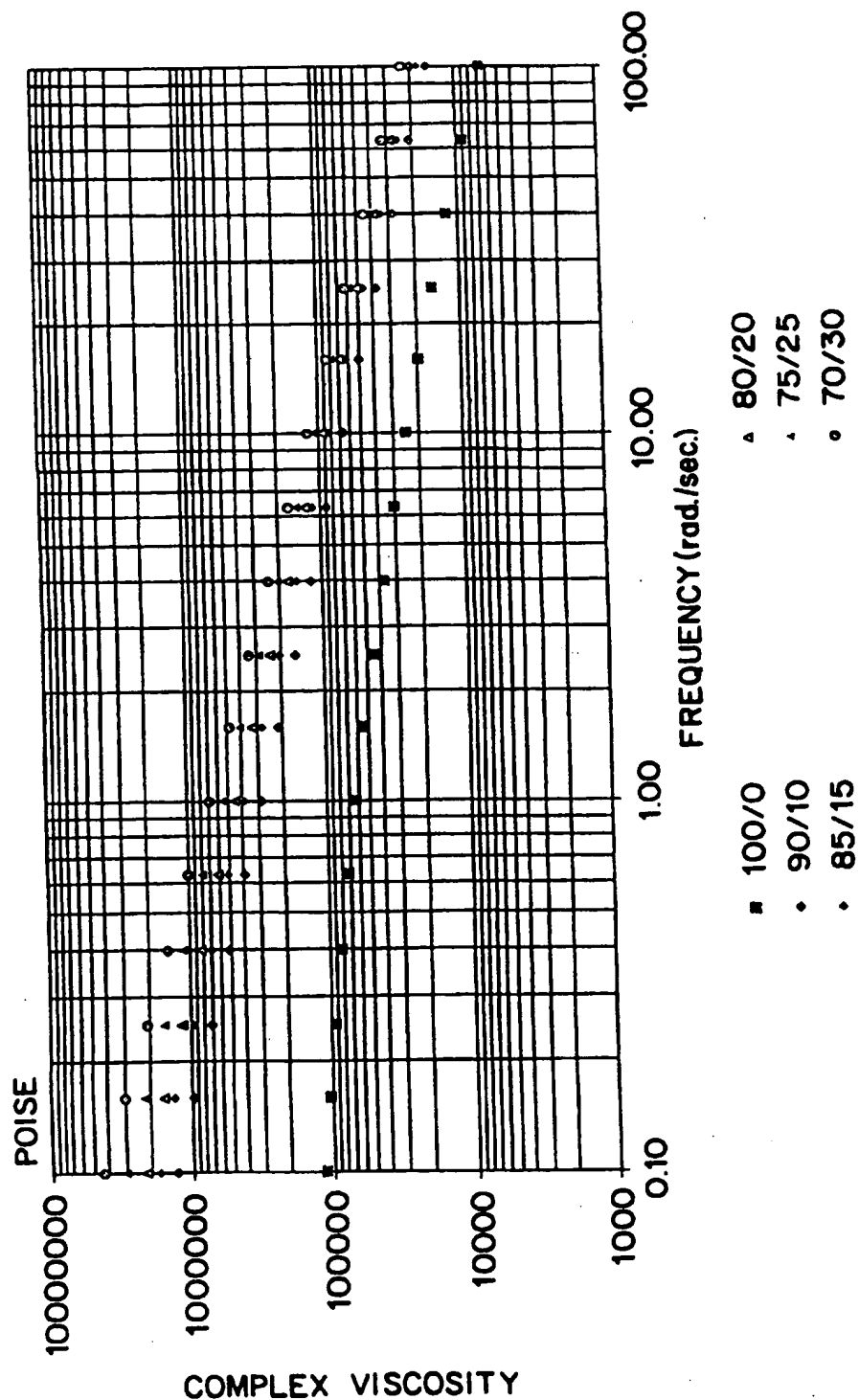
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FIG. 5



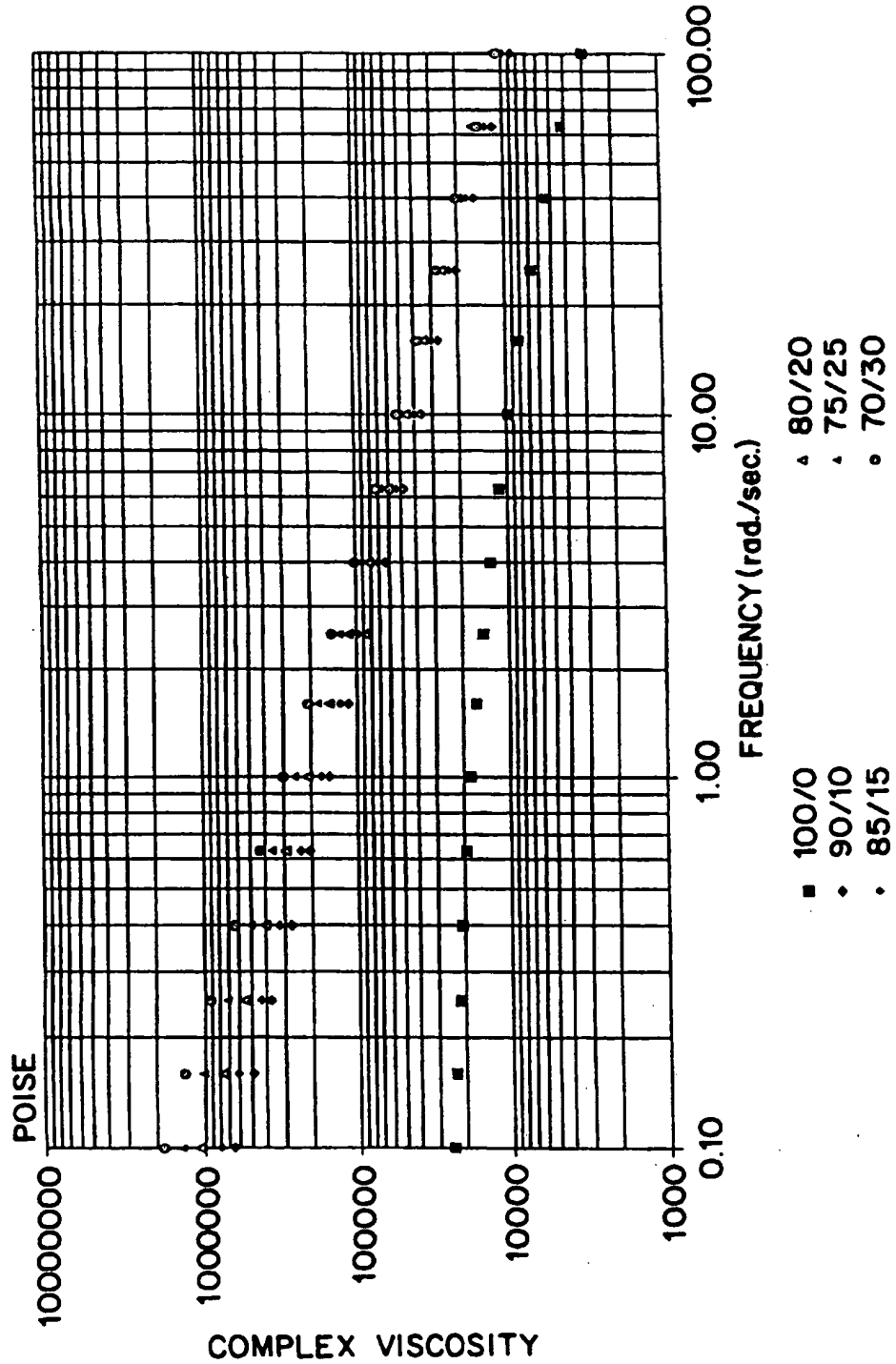
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FIG. 6



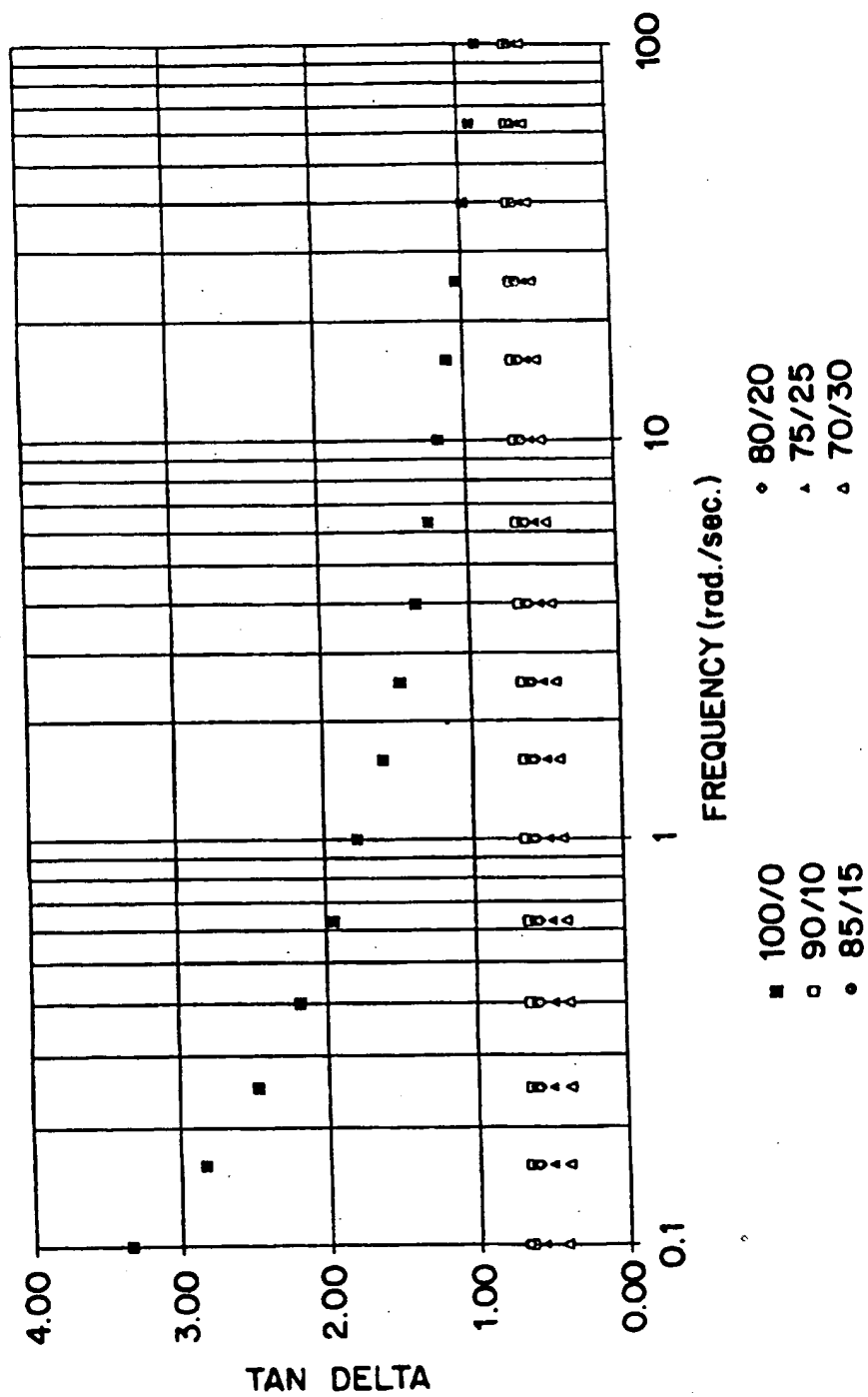
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FIG. 7



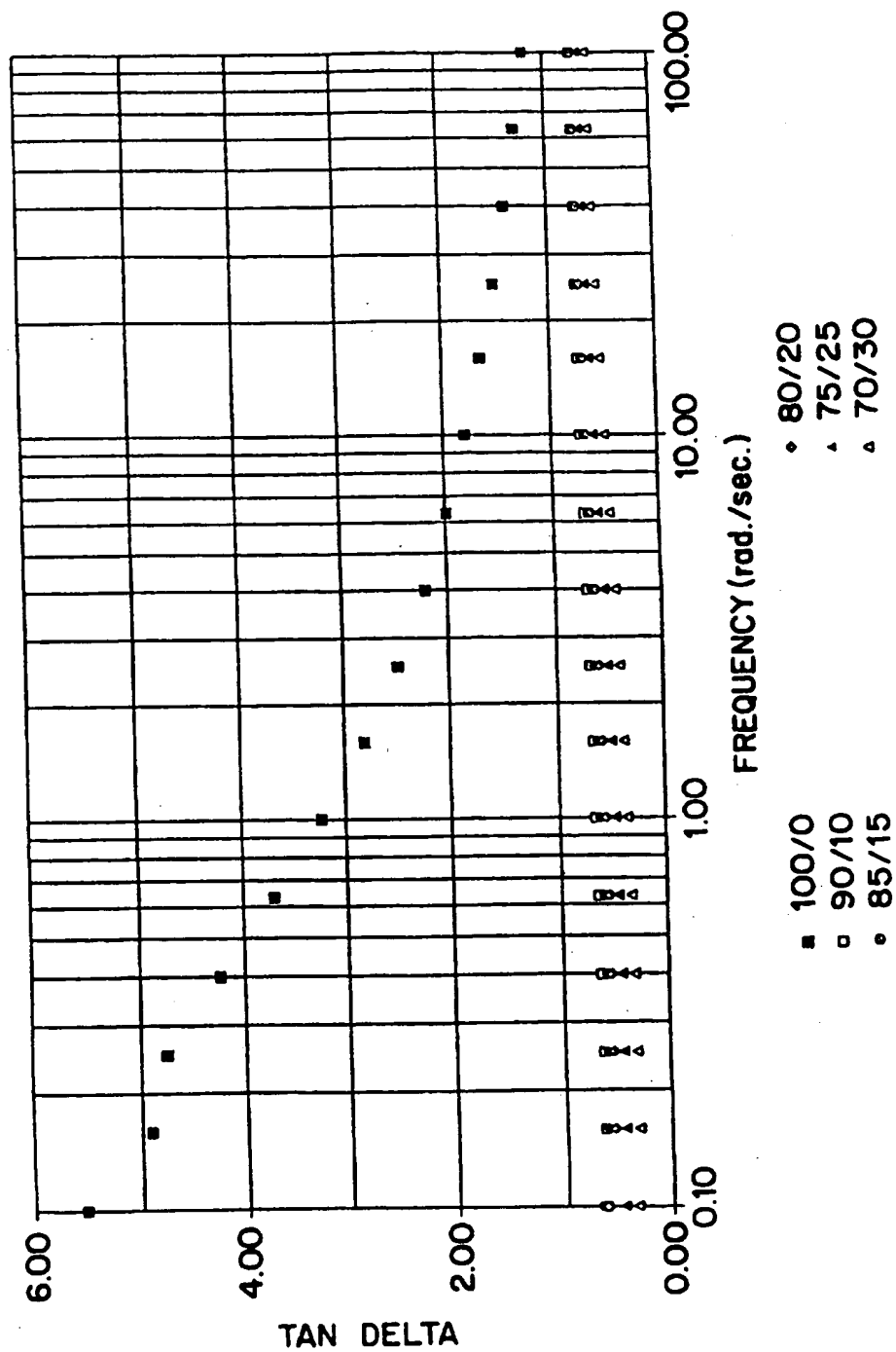
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FIG. 8



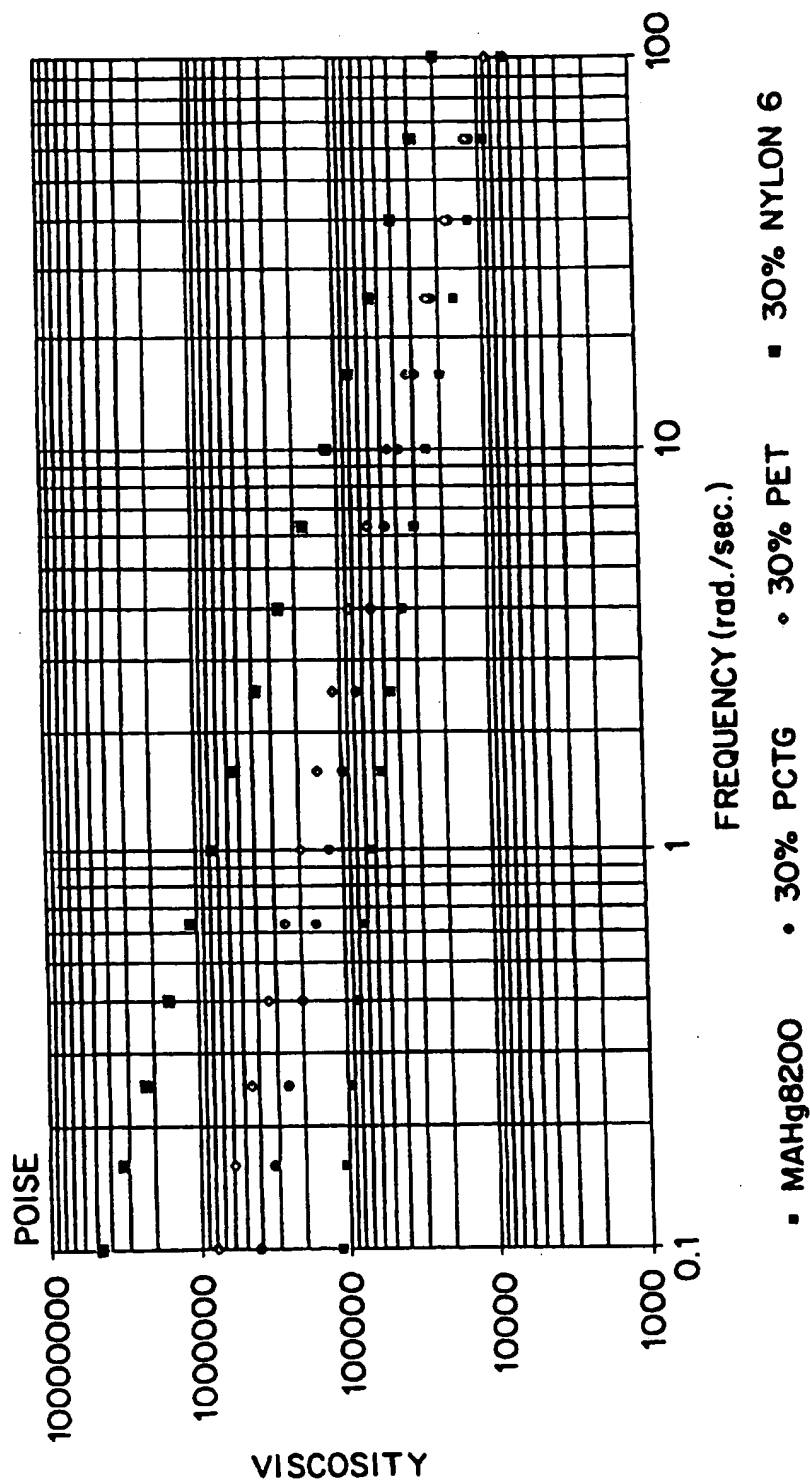
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FIG. 9



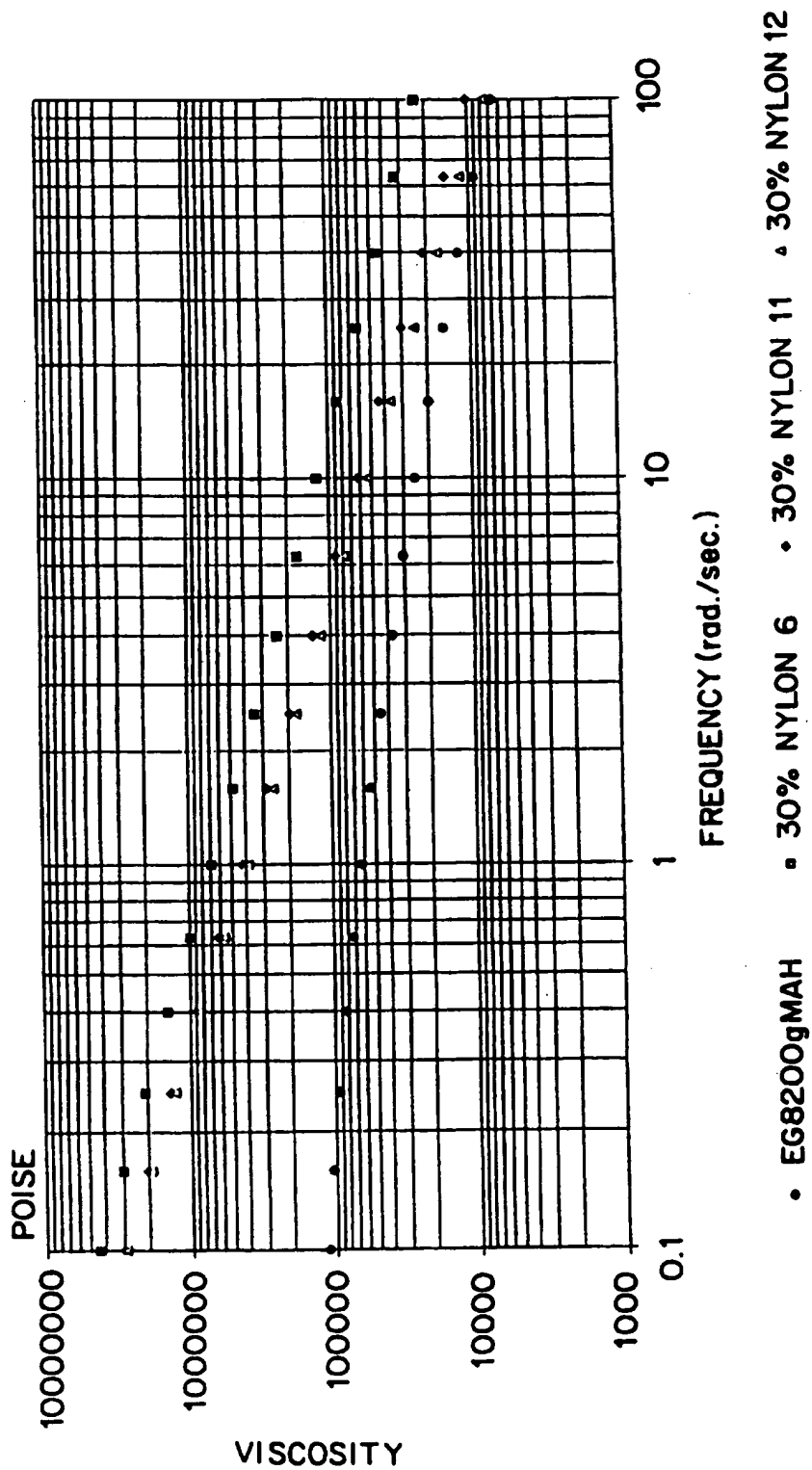
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FIG. 10



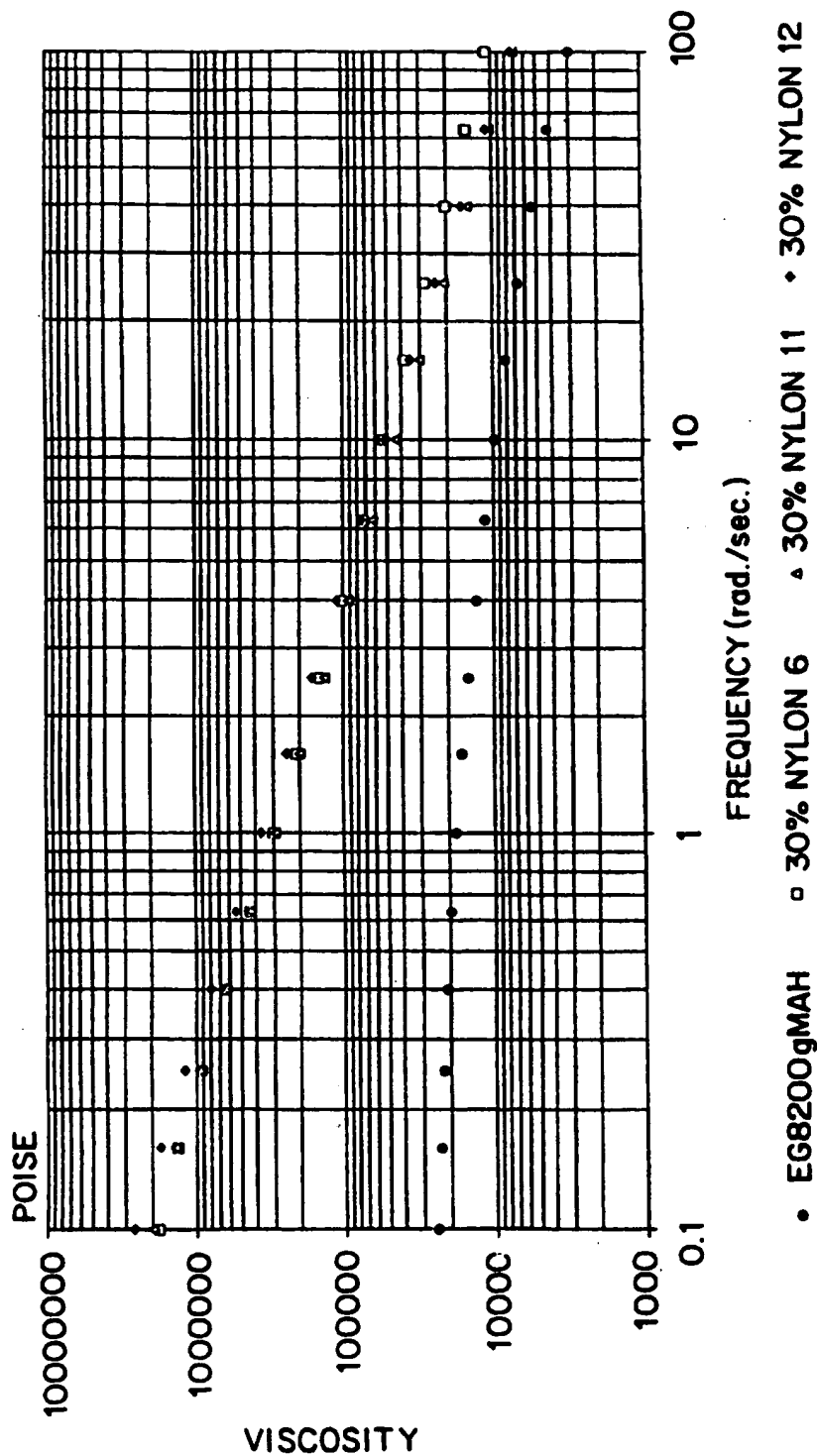
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FIG. 11



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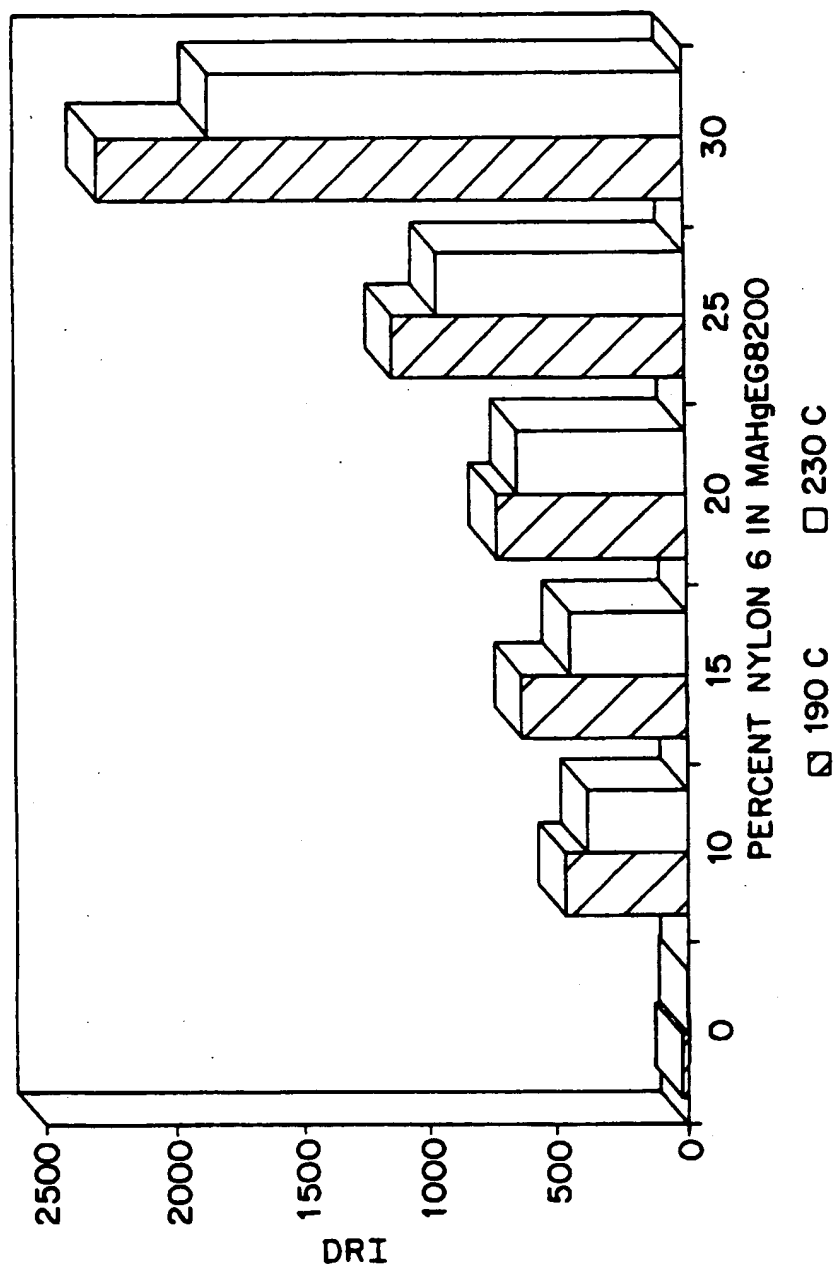
FIG. 12





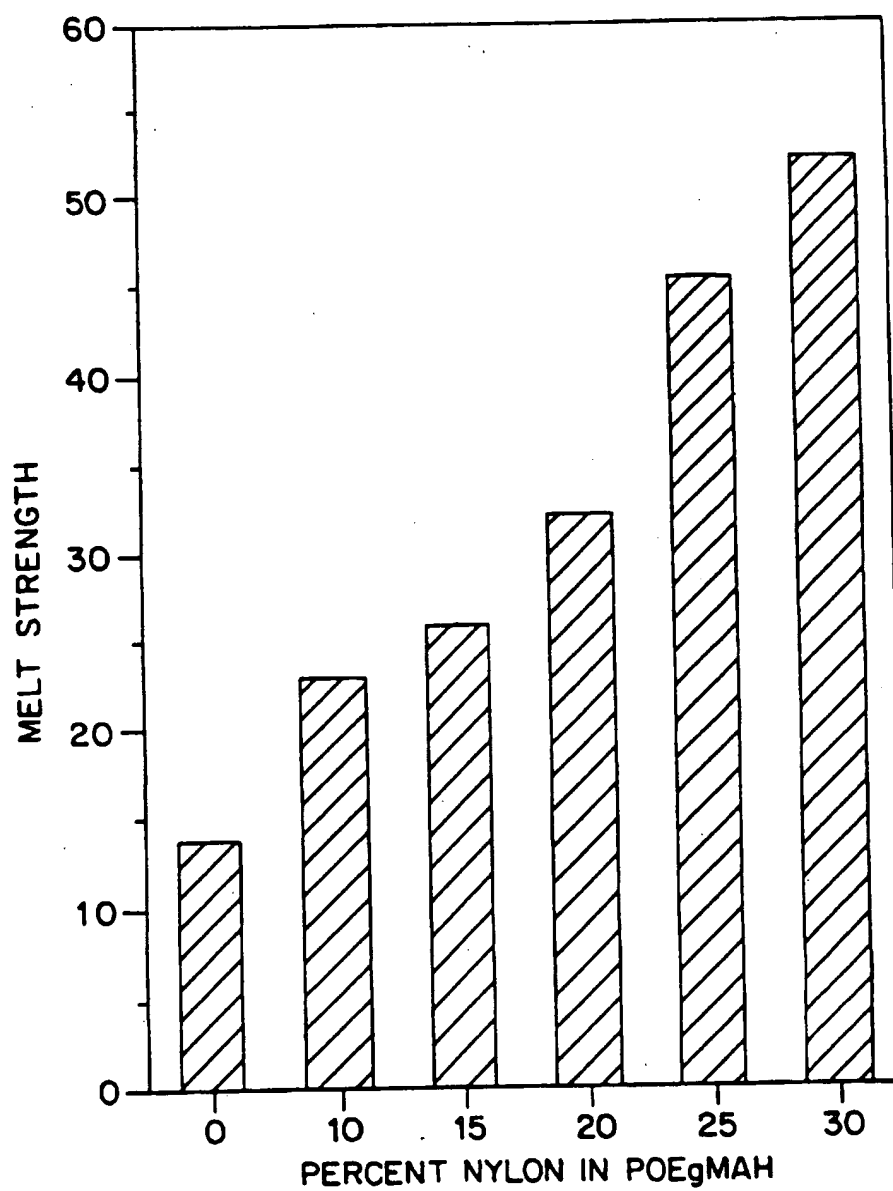
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FIG. 13



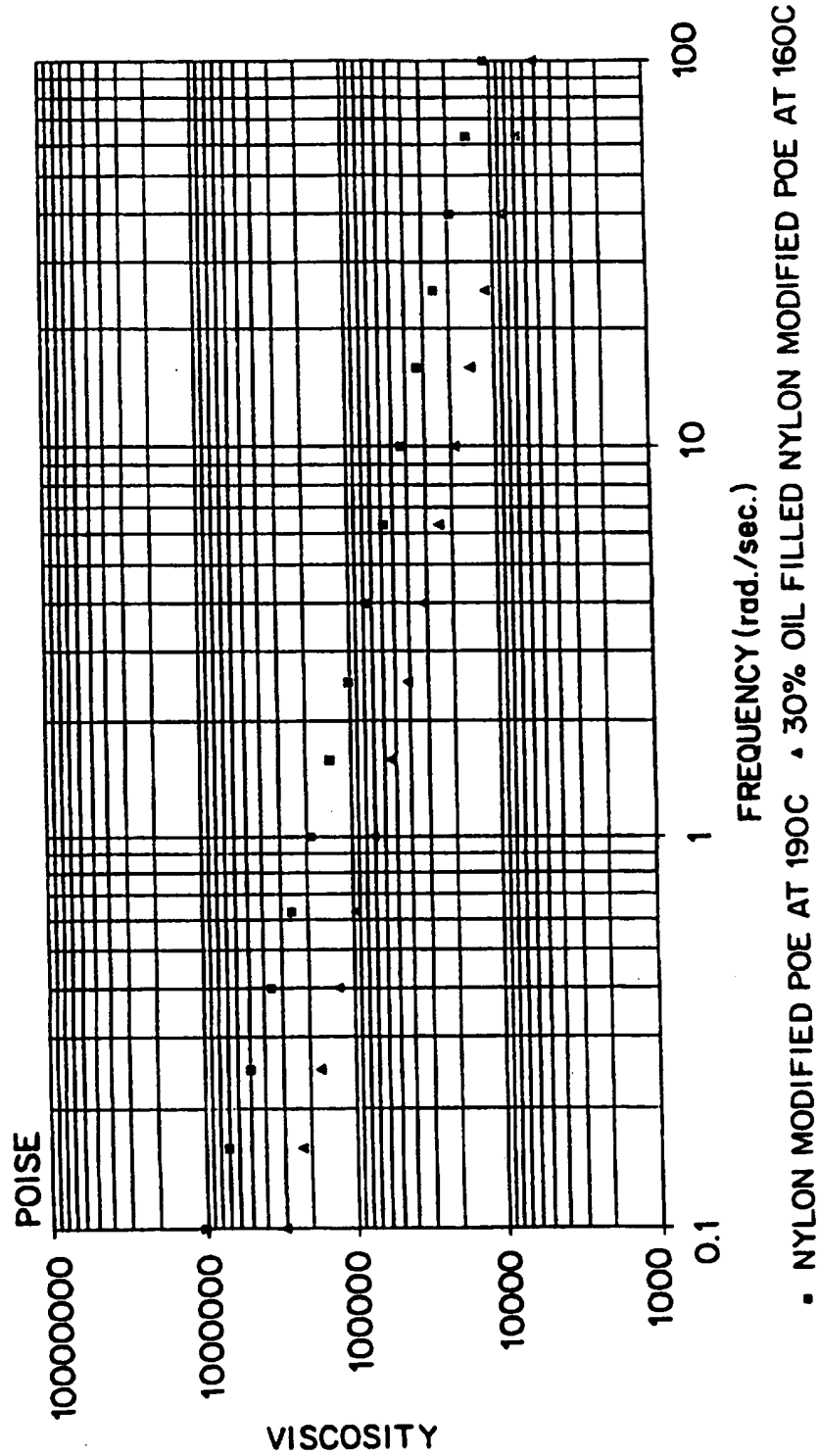
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FIG. 14



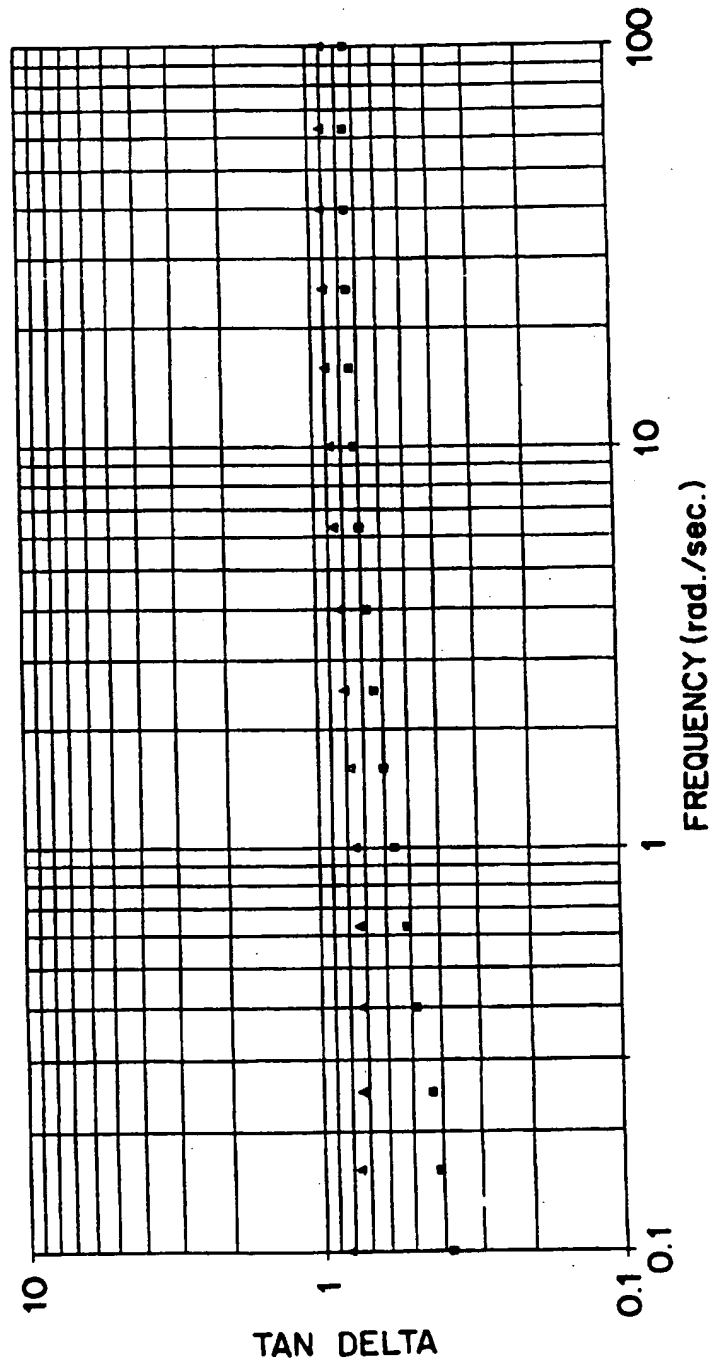
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FIG. 15



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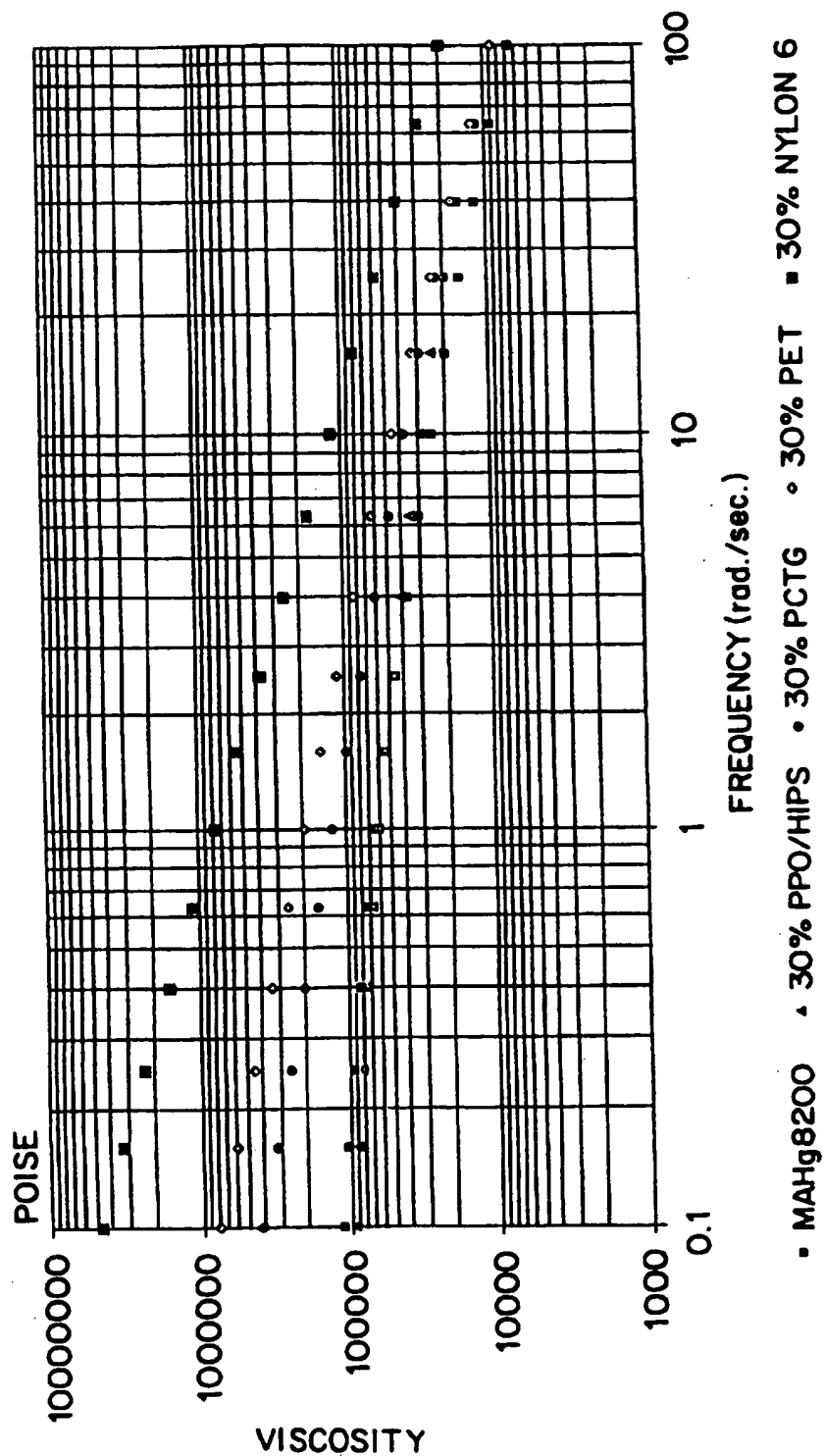
FIG. 16



- NYLON MODIFIED POE AT 190C
- ▲ 30% OIL FILLED NYLON MODIFIED POE AT 160C

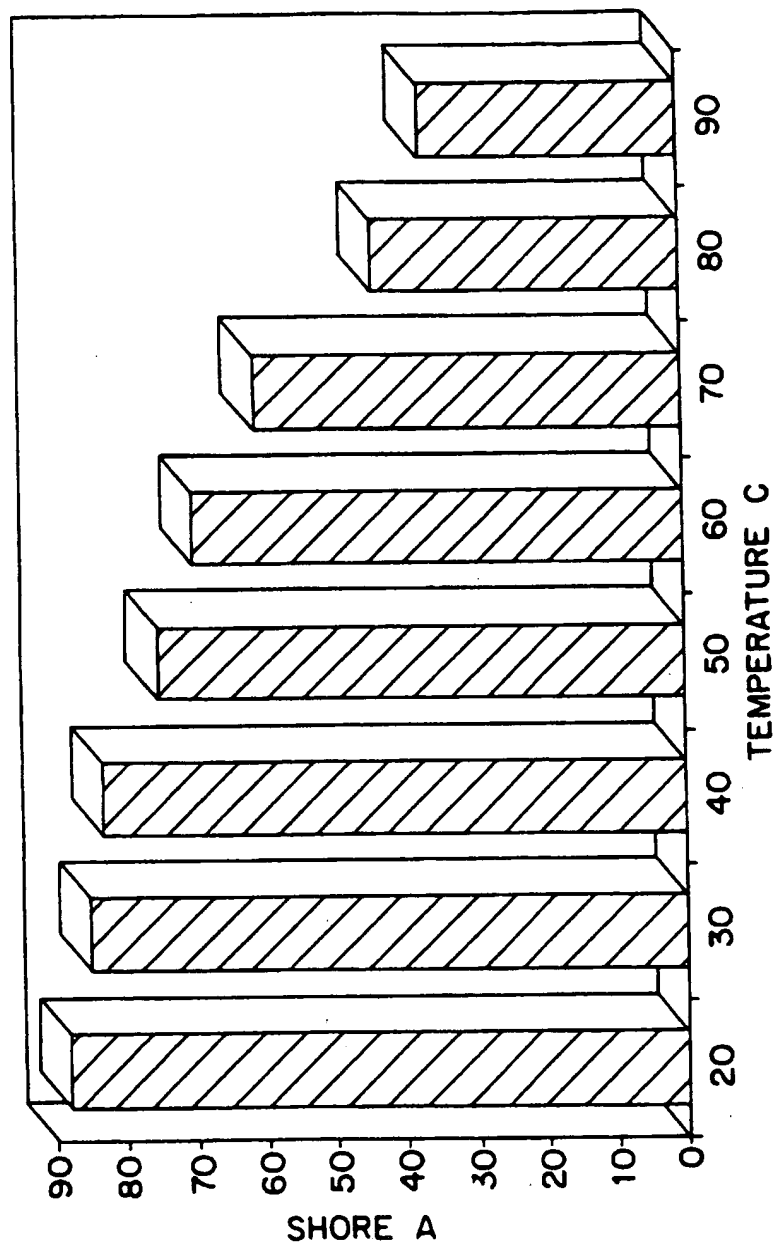
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FIG. 17



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FIG. 18



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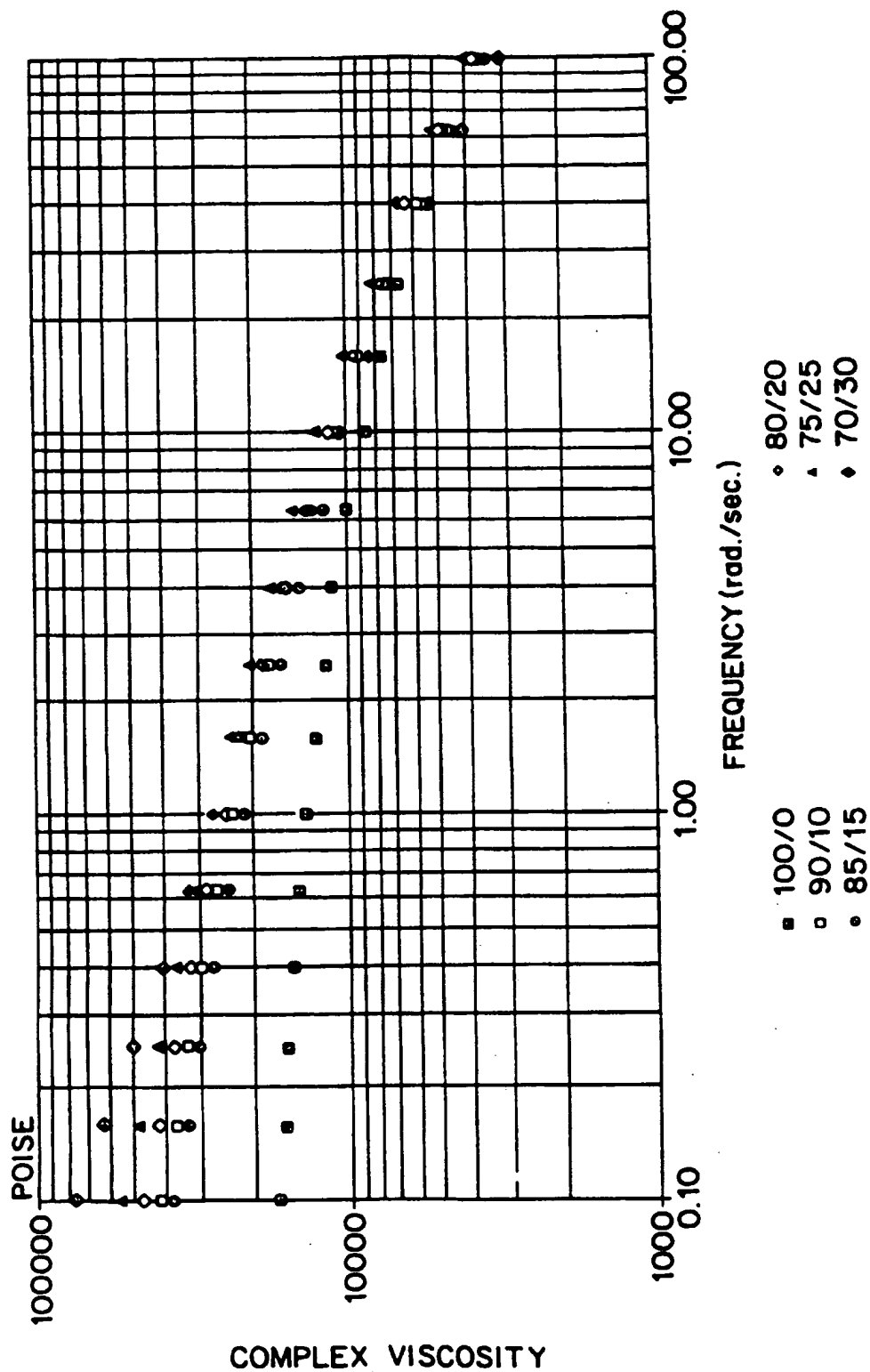
FIG. 19

Sample	Max Strain (%)	Max. Stress (PSI)	Toughness (in-lb/in)
ITP-g-MAH/PBT	2000	2700	29400
ITP*	1800	1600	14800

\*Ethylene octene copolymer with 1 MI and density of 0.87g/ml

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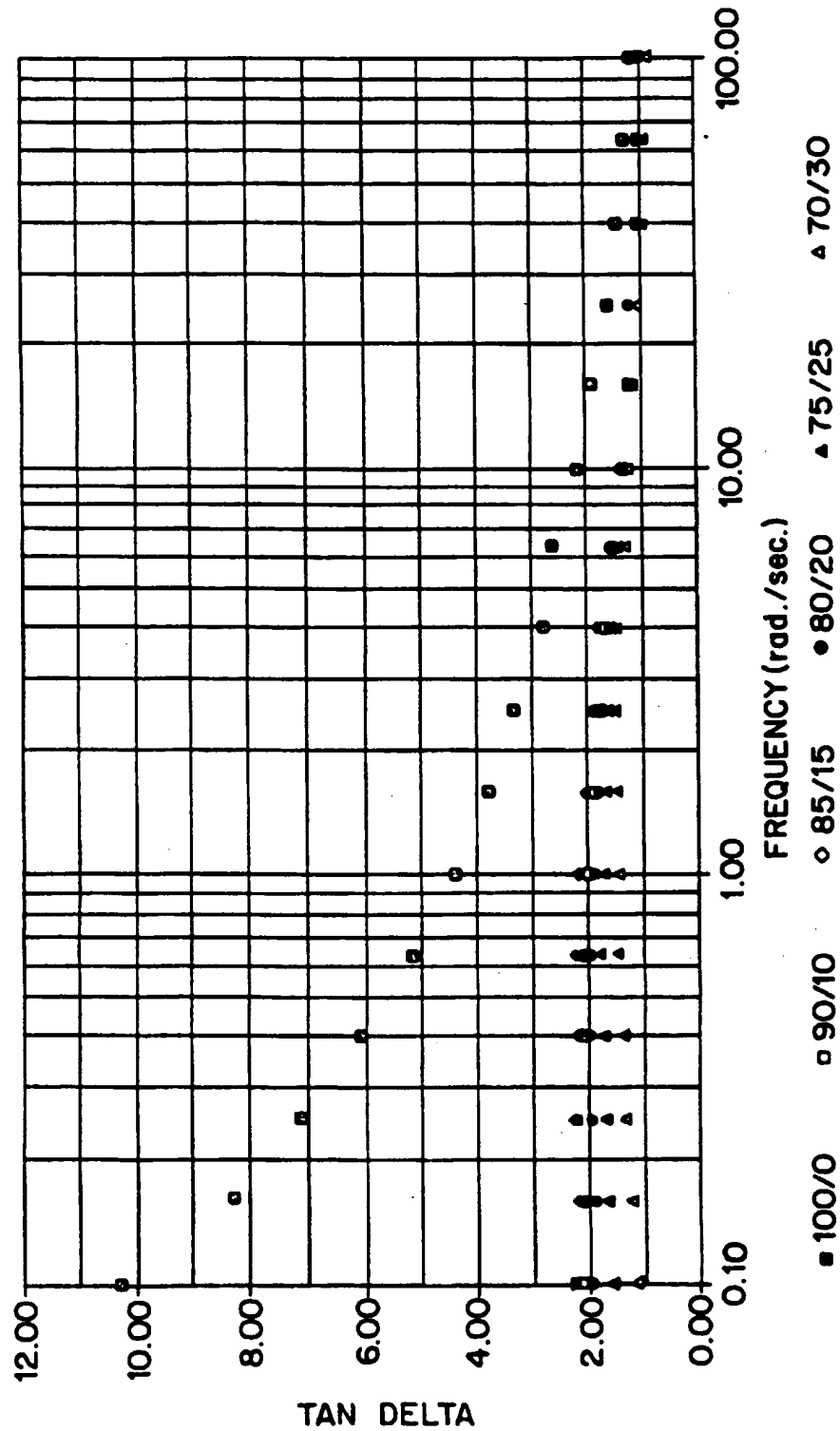
FIG. 20





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FIG. 21



# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 96/13060

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08F8/00 C08G81/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08F C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,95 17466 (BOREALIS HOLDING A/S) 29 June 1995 see the whole document ---	1-35
Y	EP,A,0 492 976 (POLYPLASTICS CO., LTD.) 1 July 1992 see the whole document ---	1-35
Y	EP,A,0 186 060 (GENERAL ELECTRIC COMPANY) 2 July 1986 see the whole document ---	1-35
Y	EP,A,0 495 099 (MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 22 July 1992 cited in the application see the whole document ---	1-35
-/-		

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

23 January 1997

Date of mailing of the international search report

10.02.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
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International Application No  
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